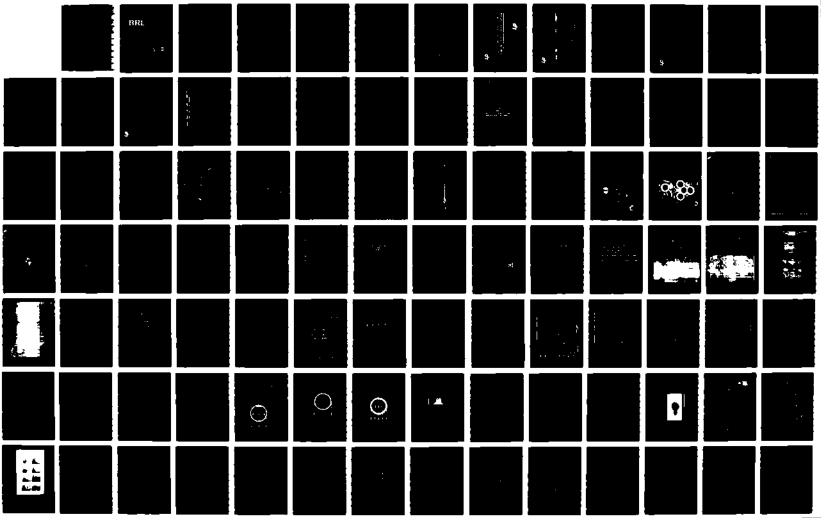
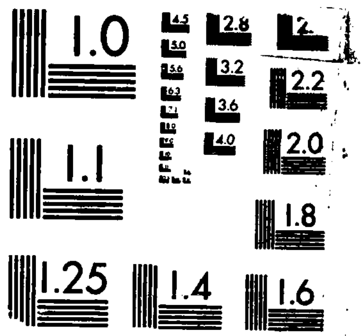
AD-A194 679 THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS 1/3
(3RD) HELD IN ABERD..(U) ARMY BALLISTIC RESEARCH LAB
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL. MAR 88
UNCLASSIFIED BRL-SP-73 F/G 19/1 NL





MICROCOPY RESOLUTION TEST CHART

UREAU OF STANDARDS-1963-A

SPECIAL PUBLICATION BRL-SP-73

BRL 1938 – Serving the Army for Fifty Years – 1988

THE THIRD ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS

ELI FREEDMAN
J. Q. WOJCIECHOWSKI

MARCH 1988

U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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ADA194679

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21	02	

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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This report contains the abstracts and viewgraphs of the 17 papers presented at the BRL's Third Annual Conference on HAN-Based Liquid Propellants. TOPICS discussed cont'd pg iii

Ballistic Research Lab

hydroxylammonium nitrate

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TABLE OF CONTENTS

contd.

TABLE OF CONTENTS (Cont.)

Contd

Keywords: Liquid gun propellants.

INTRODUCTION

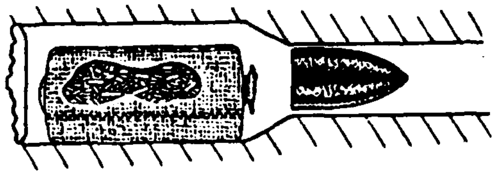
The US Army is currently investigating the use of liquid propellants (LPs) in large and medium caliber guns. These LPs are characterized by the use of hydroxylammonium nitrate (HAN) as their oxidizer. On 25-27 August 1987, the Third Annual LP Conference on HAN-Based Liquid Propellant Flames, Properties and Structure, was held at the BRL with Dr. Walter F. Morrison as General Chairman. The papers presented at this highly successful conference were given by people from academia, industry, and other government agencies.

This report is a compilation of the abstracts and viewgraphs of these papers where available. The final program is included in appendix A and a list of attendees in appendix B.

LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM

COMBUSTION CONTROL

SOLID PROPELLANT

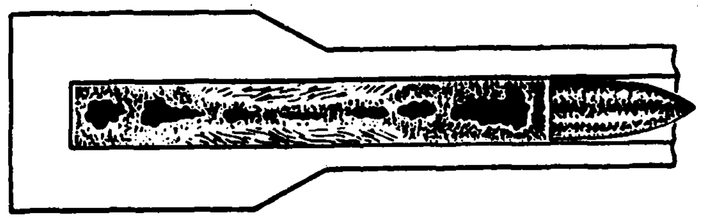


- UNDERSTOOD

BUT

- MATURE

LP BULK LOADED



- SIMPLE

BUT

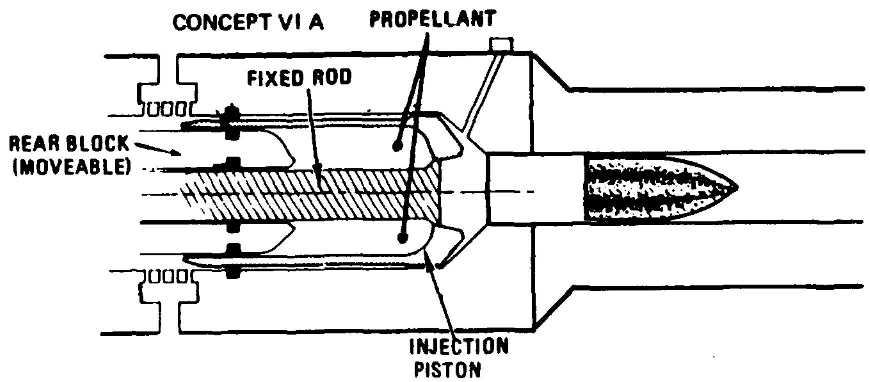
- DIFFICULT TO CONTROL

REGENERATIVE IGNITION

- BALLISTIC CONTROL

BUT

- MECHANICALLY MORE COMPLEX



LIQUID PROPELLANT
GUN
TECHNOLOGY PROGRAM

PROGRAM OBJECTIVES

- DEMONSTRATE A 'BRASSBOARD' 155mm RLPG ARTY SYSTEM IN AN M109 SPH WITH A SPECIFIC LIQUID PROPELLANT
  - BALLISTICALLY VIABLE
  - MILITARILY PRACTICAL

- DEVELOP TECHNOLOGY BASE REQUIRED TO TAKE SYSTEM INTO FSD
  - HAN-BASED LIQUID PROPELLANT

    FORMULATION
    CHARACTERIZATION
    PRODUCIBILITY
    PACKAGING AND HANDLING

  - REGENERATIVE LPG

    BASIC DESIGN PRINCIPLES & METHODOLOGY
    COMPONENT TECHNOLOGY
    DEMONSTRATED BALLISTIC PERFORMANCE
    RAM & PRODUCIBILITY DATA (LIMITED)
    SPECIFIC 'PROTOTYPE' DESIGN

  - SYSTEM INTEGRATION

    M108/9 EXPERIENCE
    INITIATE ILS ACTIVITIES
    INVOLVE DEVELOPMENT COMMUNITY
    PAPER CONCEPT STUDIES

LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM

PROGRAM MANAGEMENT

W.F. MORRISON, PROGRAM MANAGER
C.DALY, DEPUTY PROGRAM MANAGER

PROGRAM SUPPORT

R. KOPMANN
J. IRIZARRY
MAJ. R. ARNONE
N. GERIANOS
T. RINGWOOD
CPT. H. HUMPHREY

JMCA

PROPELLANT DEVELOPMENT

C. LEVERITT
D. DOWNS

TECHNOLOGY & CHARACTERIZATION

BRL
ARDEC
ARO
SNL
LLNL
FT. BELVOIR
BWL
MBRDL
SUNSTRAND
PCRL
BATTELLE
HAZARDS RESEARCH

JHU
U OF DEL
U OF MO, KC
U OF IL, CHICAGO
YALE
U OF MICHIGAN
RPI
ICT
EMI-AFB
SWRI

PACKAGING & LOGISTICS

ARDEC
PM AMMO LOG
BELL AEROSPACE
JPL

LP PRODUCTION

BRL
ARDEC
PBM
NOSIH

OLIN
THIOKOL
BATTELLE

GUN DEVELOPMENT

J. KNAPTON
R. KOPMANN

INTERIOR BALLISTICS

BRL
ARDEC
ARO
P. GOUGH, ASSOC.
SAIC

155mm GUN DEVELOPMENT

GEOSD
GEA&ESD
BWL/WVA
CSTA
MTL

SYSTEMS APPLICATIONS

T. POTTHOFF
R. KOPMANN
T. RINGWOOD
CPT. H. HUMPHREY

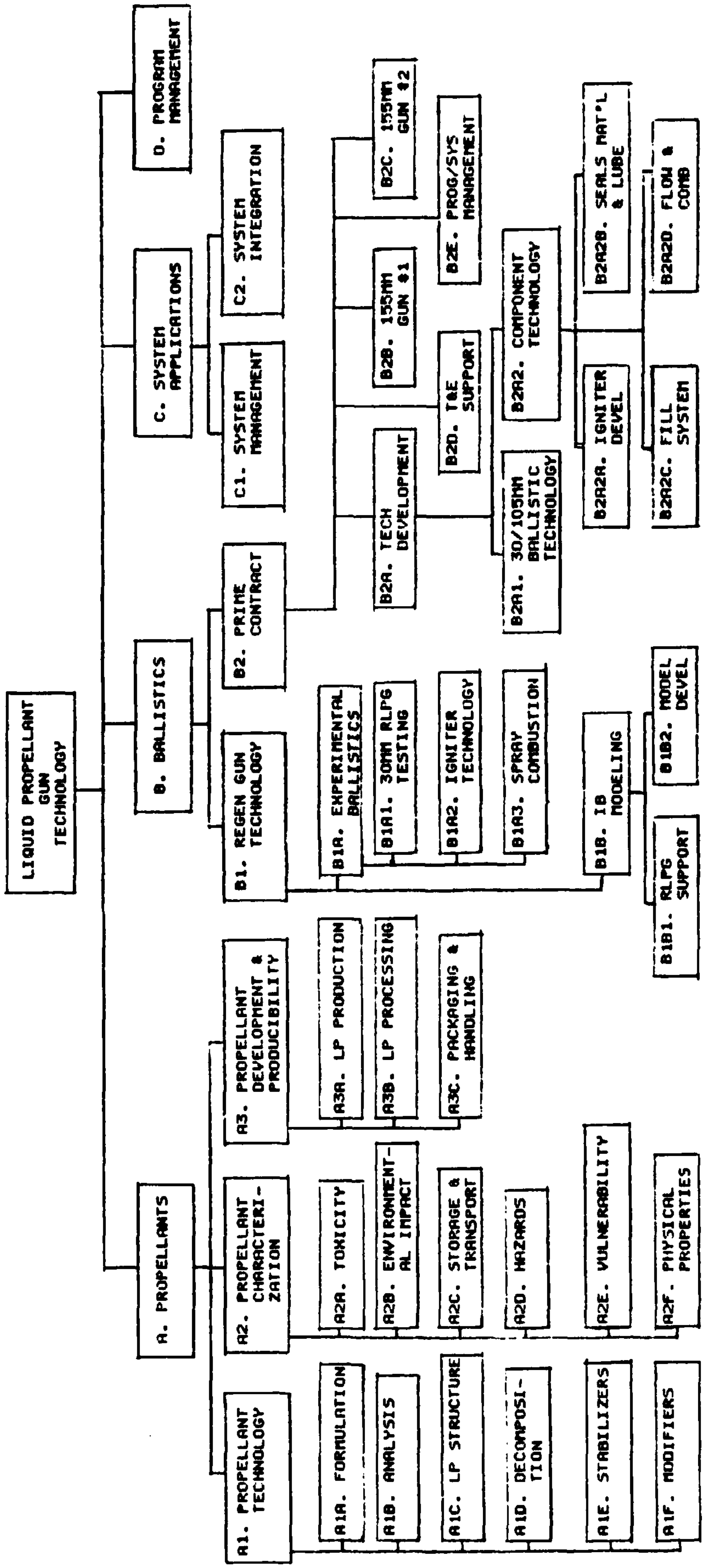
SYSTEM INTEGRATION

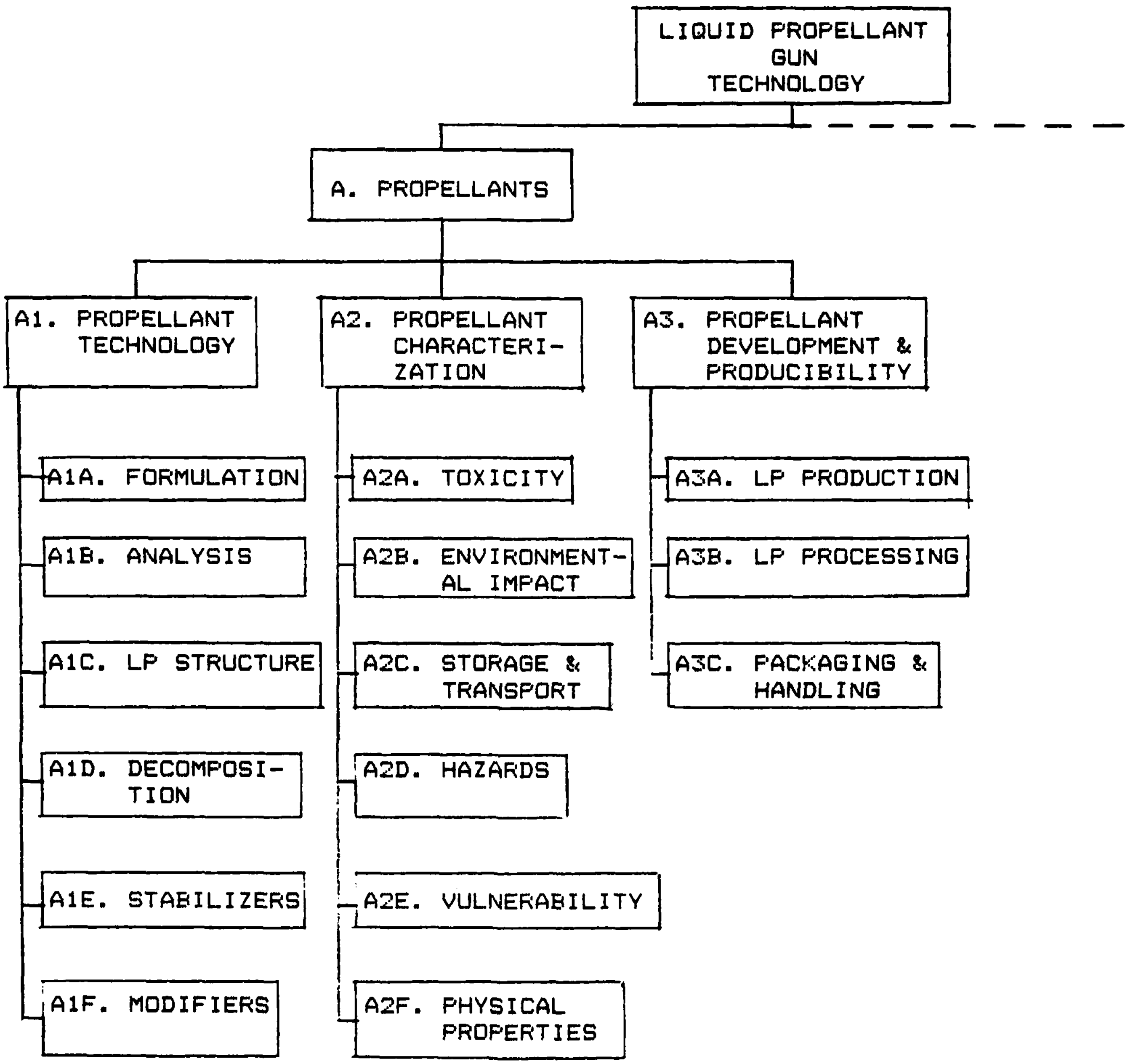
ARDEC
GEOSD
LETTERKENNY

SYSTEM MANAGEMENT

ARDEC
GEOSD

- JOINT LABCOM - ARDEC PROGRAM
- EXTENSIVE INDUSTRY & ACEDEMIC PARTICIPATION


LIQUID PROPELLANT GUN TECHNOLOGY
A. PROPELLANTS
B. BALLISTICS
C. SYSTEM APPLICATIONS
D. PROGRAM MANAGEMENT
A1. PROPELLANT TECHNOLOGY
A2. PROPELLANT CHARACTERIZATION
A3. PROPELLANT DEVELOPMENT & PRODUCIBILITY
A1A. FORMULATION
A1B. ANALYSIS
A1C. LP STRUCTURE
A1D. DECOMPOSITION
A1E. STABILIZERS
A1F. MODIFIERS
A2A. TOXICITY
A2B. ENVIRONMENTAL IMPACT
A2C. STORAGE & TRANSPORT
A2D. HAZARDS
A2E. VULNERABILITY
A2F. PHYSICAL PROPERTIES
A3A. LP PRODUCTION
A3B. LP PROCESSING
A3C. PACKAGING & HANDLING
B1. REGEN GUN TECHNOLOGY
B2. PRIME CONTRACT
B1A. EXPERIMENTAL BALLISTICS
B1A1. 30MM RLPG TESTING
B1A2. IGNITER TECHNOLOGY
B1A3. SPRAY COMBUSTION
B1B. IB MODELING
B1B1. RLPG SUPPORT
B1B2. MODEL DEVEL
B2A. TECH DEVELOPMENT
B2B. 155MM GUN #1
B2C. 155MM GUN #2
B2D. T&E SUPPORT
B2E. PROG/SYS MANAGEMENT
B2A1. 30/105MM BALLISTIC TECHNOLOGY
B2A2. COMPONENT TECHNOLOGY
B2A2A. IGNITER DEVEL
B2A2B. SEALS MAT'L & LUBE
B2A2C. FILL SYSTEM
B2A2D. FLOW & COMB
C1. SYSTEM MANAGEMENT
C2. SYSTEM INTEGRATION


LIQUID PROPELLANT GUN TECHNOLOGY
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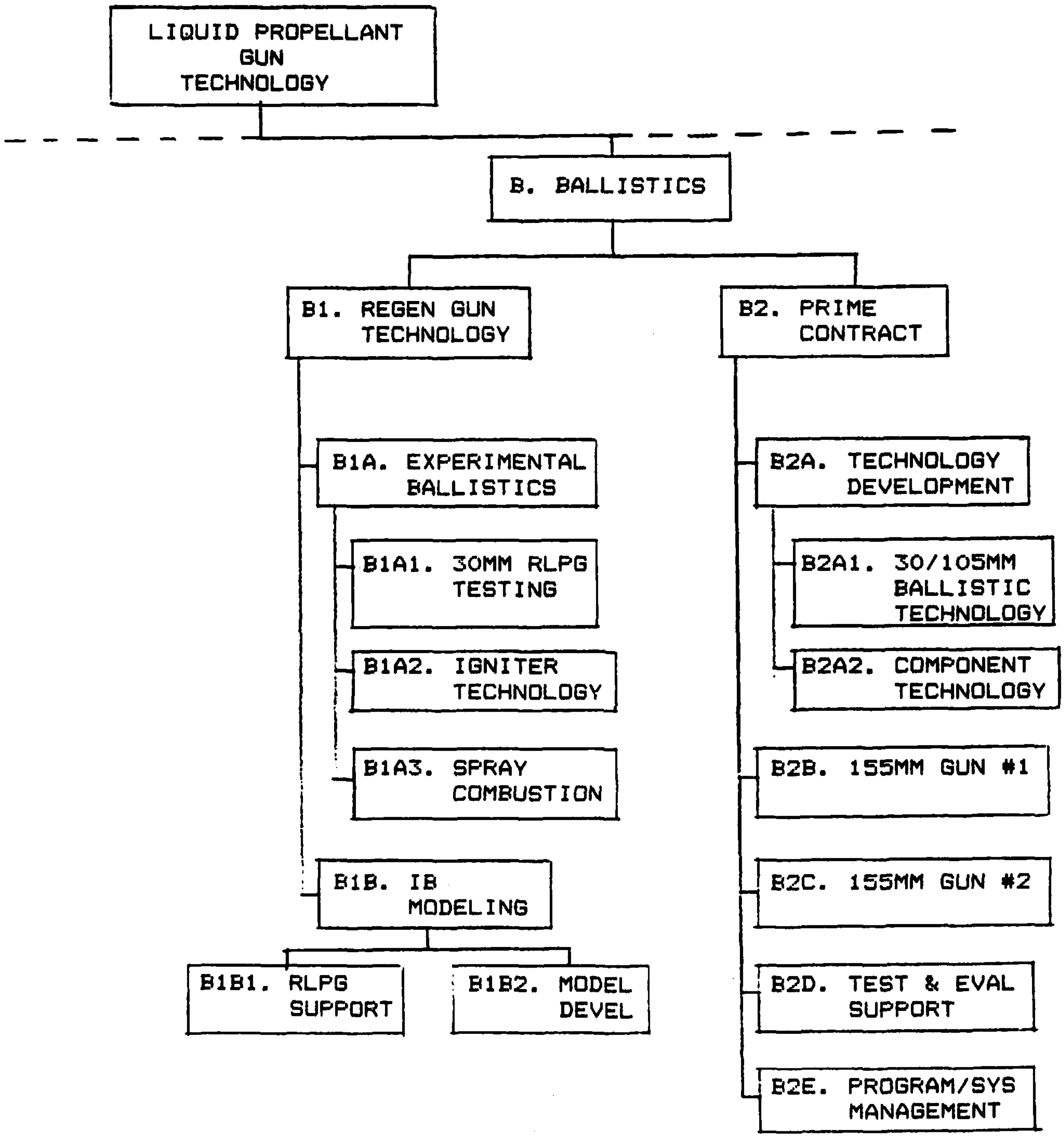
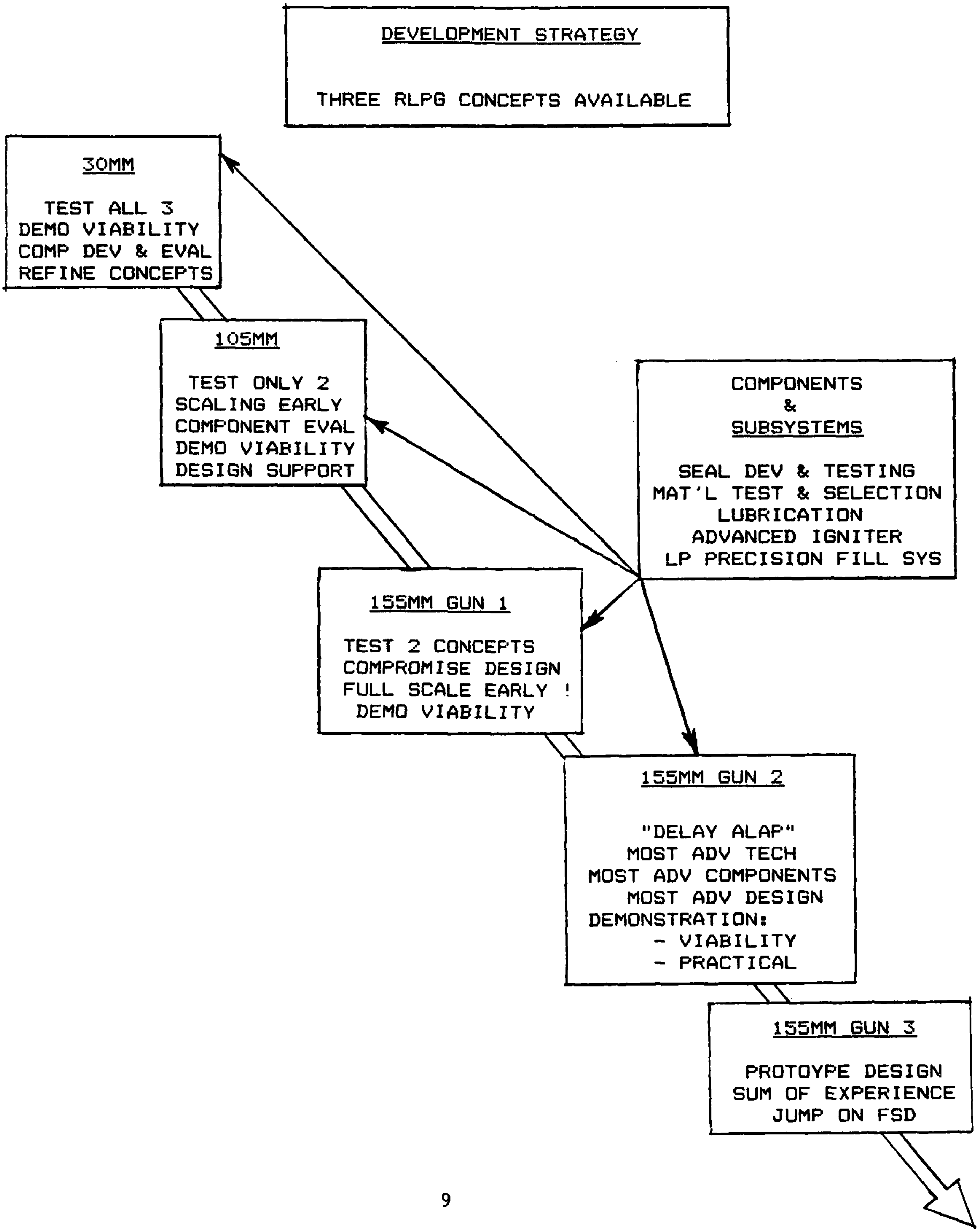
A1. PROPELLANT TECHNOLOGY
A2. PROPELLANT CHARACTERI-ZATION
A3. PROPELLANT DEVELOPMENT & PRODUCIBILITY
A1A. FORMULATION
A1B. ANALYSIS
A1C. LP STRUCTURE
A1D. DECOMPOSI-TION
A1E. STABILIZERS
A1F. MODIFIERS
A2A. TOXICITY
A2B. ENVIRONMENT-AL IMPACT
A2C. STORAGE & TRANSPORT
A2D. HAZARDS
A2E. VULNERABILITY
A2F. PHYSICAL PROPERTIES
A3A. LP PRODUCTION
A3B. LP PROCESSING
A3C. PACKAGING & HANDLING


LIQUID PROPELLANT GUN TECHNOLOGY
B. BALLISTICS
B1. REGEN GUN TECHNOLOGY
B2. PRIME CONTRACT
B1A. EXPERIMENTAL BALLISTICS
B1A1. 30MM RLPG TESTING
B1A2. IGNITER TECHNOLOGY
B1A3. SPRAY COMBUSTION
B1B. IB MODELING
B1B1. RLPG SUPPORT
B1B2. MODEL DEVEL
B2A. TECHNOLOGY DEVELOPMENT
B2A1. 30/105MM BALLISTIC TECHNOLOGY
B2A2. COMPONENT TECHNOLOGY
B2B. 155MM GUN #1
B2C. 155MM GUN #2
B2D. TEST & EVAL SUPPORT
B2E. PROGRAM/SYS MANAGEMENT


DEVELOPMENT STRATEGY
THREE RLPG CONCEPTS AVAILABLE
30MM
TEST ALL 3
DEMO VIABILITY
COMP DEV & EVAL
REFINE CONCEPTS
105MM
TEST ONLY 2
SCALING EARLY
COMPONENT EVAL
DEMO VIABILITY
DESIGN SUPPORT
COMPONENTS
&
SUBSYSTEMS
SEAL DEV & TESTING
MAT'L TEST & SELECTION
LUBRICATION
ADVANCED IGNITER
LP PRECISION FILL SYS
155MM GUN 1
TEST 2 CONCEPTS
COMPROMISE DESIGN
FULL SCALE EARLY !
DEMO VIABILITY
155MM GUN 2
"DELAY ALAP"
MOST ADV TECH
MOST ADV COMPONENTS
MOST ADV DESIGN
DEMONSTRATION:
- VIABILITY
- PRACTICAL
155MM GUN 3
PROTOYPE DESIGN
SUM OF EXPERIENCE
JUMP ON FSD

CURRENT ARMY PROGRAM

ACCELERATED D-155

1ST GENERATION: 155 mm TEST FY 88

2ND GENERATION: 155 mm TEST FY 89

- CONTINUOUS ZONING
- BURST FIRE

COMPONENT DEVELOPMENT

800 TO 1000 ROUNDS IN 155 mm

3RD GENERATION DESIGN FOR FSD

– TECHNICAL MATURITY TO SUPPORT FSD –

GE CONTRIBUTION

PROJECTILE AUTOLOADER

FIRE CONTROL

TURRET ELEVATION DRIVES

VEHICLE INTEGRATION

– SYSTEM LEVEL GROUNDWORK – FOR FUTURE DEVELOPMENT

LP WEAPONIZATION DEMO

155 mm RLPG CANNON MOUNTED ON SPH

MUZZLE VELOCITY: 210 TO 825 m/s

RATE OF FIRE: 3 TO 10rds min

BURST FIRE DEMONSTRATION

3 ROUNDS TIME-ON-TARGET

– LP IN ADVANCED INDIRECT FIRE ROLE–

LIQUID PROPELLANT GUN TECHNOLOGY
TECHNICAL RISKS AND UNKNOWNS

PROPELLANT

- HIGH TEMPERATURE
- CONTAMINATION

RLPG

- RELIABILITY AND MAINTAINABILITY (RLPG MORE COMPLEX)
  - SEAL LIFE
  - COMPONENT DEVELOPMENT
- SCALING FROM 105MM to 155MM

MAY 86

ABSTRACT

SOLID + LIQUID PHASE EQUILIBRIUM FOR THE WATER + HYDROXYLAMMONIUM NITRATE SYSTEM

by
J. Bevan Ott and Johanne Artman
Department of Chemistry
Brigham Young University
Provo, Utah

The binary solid + liquid phase diagram has been measured for the water + hydroxylammonium nitrate (HAN) system. The phase diagram is a simple eutectic system with the eutectic at 231.5 K (-41.7°C) and a mole fraction of HAN of 0.281 (wt fraction of HAN = 0.676). The phase diagrams expressed in terms of mole fraction x and weight fraction f are shown in figures 1 and 2.

The enthalpy of fusion of the HAN was determined from the solid + liquid results to be 11 ± 2 J/mol. The HAN was obtained from Southwestern Analytical Chemicals, Inc. as an approximately 2.8 molar solution. The water was removed by vacuum drying over a three month time period, but the sample was still not pure. We estimate the impurity level from the change in melting temperature with fraction melted to be 0.040 mole fraction. We are at present trying to determine the nature of the impurity.

We obtained a melting temperature for the impure sample of HAN of 315.95 K (42.7°C). The melting point corrected to zero impurity would be 317.7 K (44.5°C).

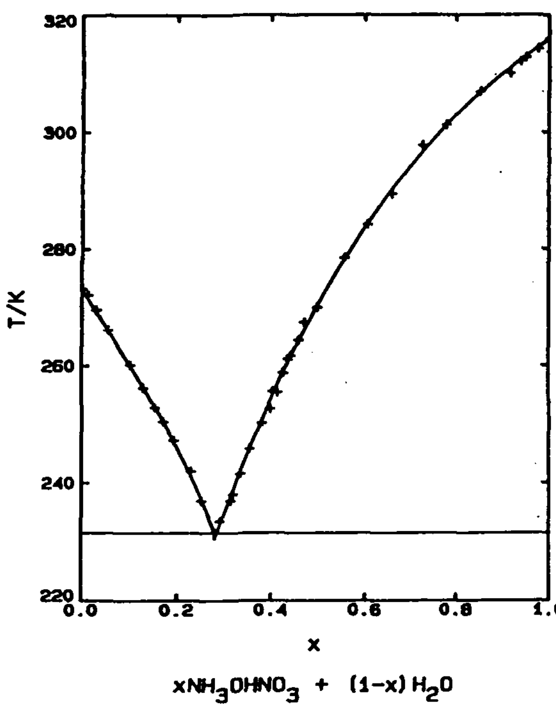


Figure 1. Solid + liquid-phase diagram for HAN + water expressed in terms of Kelvin temperature vs. mole fraction HAN

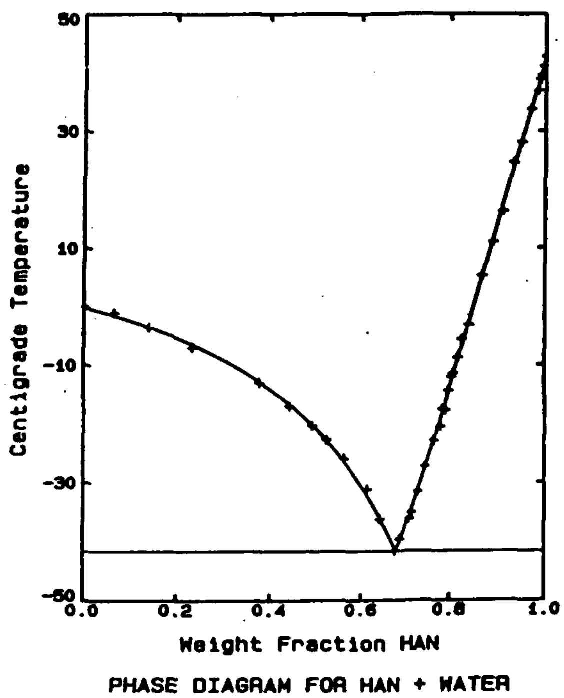


Figure 2. Solid + liquid-phase diagram for HAN + water expressed in terms of centigrade temperature vs. weight fraction HAN

DIFFRACTION STUDIES OF HAN

F. K. Ross and Q. Xie
Research Reactor
University of Missouri
Columbia, MO 65211
(314-882-5237)

The objective of this research program has been to provide information about the structures of crystalline and liquid HAN. To this end, we developed techniques for crystallizing HAN, determined the structure of the crystalline material by X-ray diffraction(1), improved the structural model by providing a single crystal neutron diffraction study(2) and during the past year have concentrated on measuring the diffraction from liquid samples. The crystal data is used to develop a description for the potential of HAN, but obviously is not necessarily an ideal example of the liquid state. The liquid scattering information is intended to test the ability of the model to reproduce the measurable properties of the liquid and, in conjunction with theoretical studies, to provide a better understanding of the liquid.

Diffraction data have been acquired for HAN, for fully deuterated HAN and for a "null" isotopic mixture (64% hydrogen of scattering power -.374f and 36% deuterium of scattering power +.667f). In addition, we have continued earlier X-ray diffraction studies with the inclusion of a pyrolytic graphite crystal to produce monochromatic radiation and with the development of a liquid cell for use in the flat-plate geometry. The monochromator is necessary to produce a diffraction pattern which can be deconvoluted from the source spectrum and the latter geometry makes up for some of the intensity loss incurred. Flat-plate geometry also reduces the severity of the absorption corrections incurred for the cylindrical samples (HAN liquid in a quartz capillary tube) reported last year (2). Background scattering from the container is still a problem though, and we find rather bothersome partial crystallinity in both the thin-wall quartz tubing used for the neutron studies and in the stretched Mylar window of our new X-ray cell. Efforts to improve the removal of container scattering from the diffraction pattern are underway.

The weakness of the diffracted intensity in the X-ray experiment suggests that this work might be more appropriately performed at a synchrotron laboratory. Such an experiment is being considered, but it also requires the use of a sample cell. Our X-ray experiments are still providing much useful information to aid in planning the synchrotron experiment.

---

(1) A. L. Rheingold, J. T. Cronin, T. B. Brill and F. K. Ross, Acta Cryst., (1987).C43,402-404.

(2) F. K. Ross, Conference on HAN-Based Liquid Propellant Flames, Properties and Structure, BRL, Aberdeen Proving Grounds, July 29-31, 1986.

* Research Supported by Army Research Office grant DAAG29-85-K-0064.

DIFFRACTION STUDIES OF HAN

F. K. Ross and Q. Xie
Research Reactor
University of Missouri
Columbia, MO 65211

Research supported by the Army Research Office, "Structure, Potential Energy and Thermodynamic Properties of Hydroxylammonium Nitrate", R. D. Murphy and F. K. Ross.

OBJECTIVES

1. Crystallize HAN and determine (crystal) structure.
   a) X-ray diffraction (HAN, d4-HAN)
   b) Neutron diffraction
   c) Search for other structures or phases

2. Monte Carlo calculations (R. D. Murphy, UMKC).
   a) Generate potential from structure parameters
   b) Calculate thermodynamic properties from the potential
   c) Use potential to calculate liquid scattering (diffraction)

3. Measure liquid scattering (diffraction).
   a) Neutron - HAN, d4-HAN, 36/64% null isotope mixture
   b) X-ray

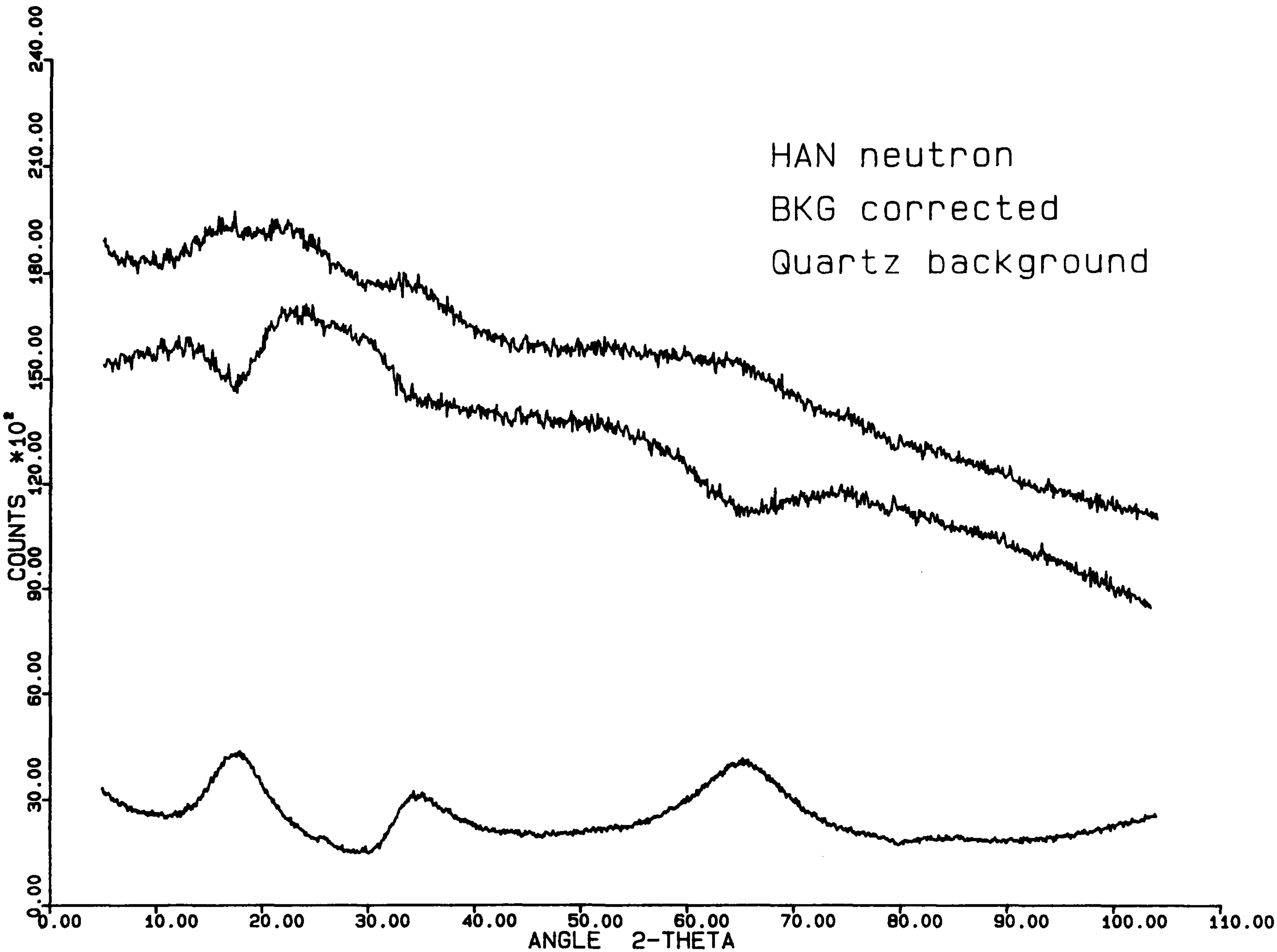
FUTURE DIRECTIONS

1. LIQUID X-RAY SCATTERING AT SHORTER WAVELENGTHS
   (Mo = 0.71 Å , Ag = 0.56 Å)

2. FOCUSSING MONOCHROMATORS

[illegible]

4. ELECTRON DENSITY ANALYSIS
   - e^- density maps
   - electrostatic potential maps
   - multipole model refinement



HAN neutron
BKG corrected
Quartz background
COUNTS *10²
ANGLE 2-THETA
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30.00
60.00
90.00
120.00
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240.00
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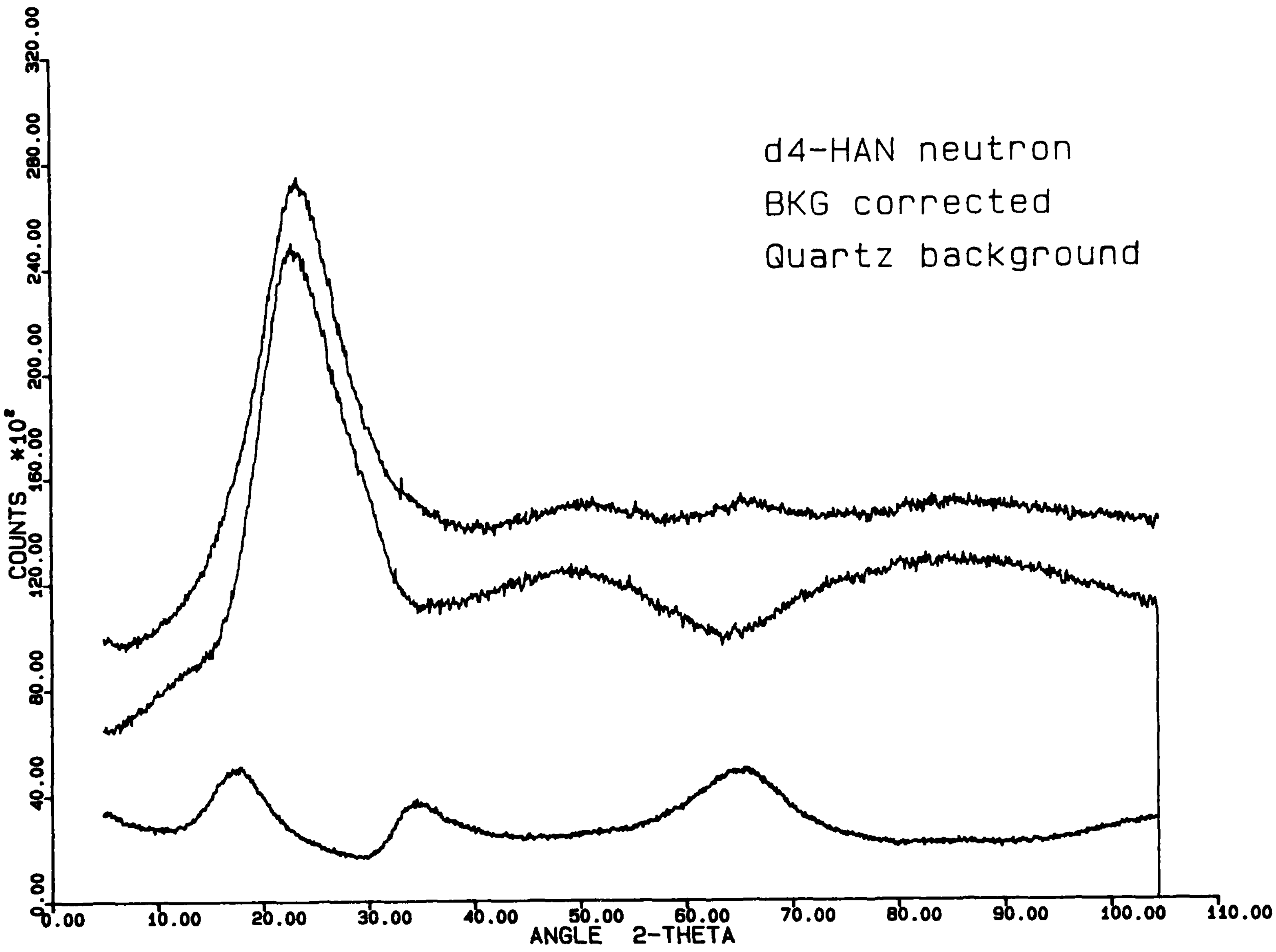
100.00
110.00


d4-HAN neutron
BKG corrected
Quartz background
COUNTS *10²
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80.00
120.00
160.00
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280.00
320.00
0.00
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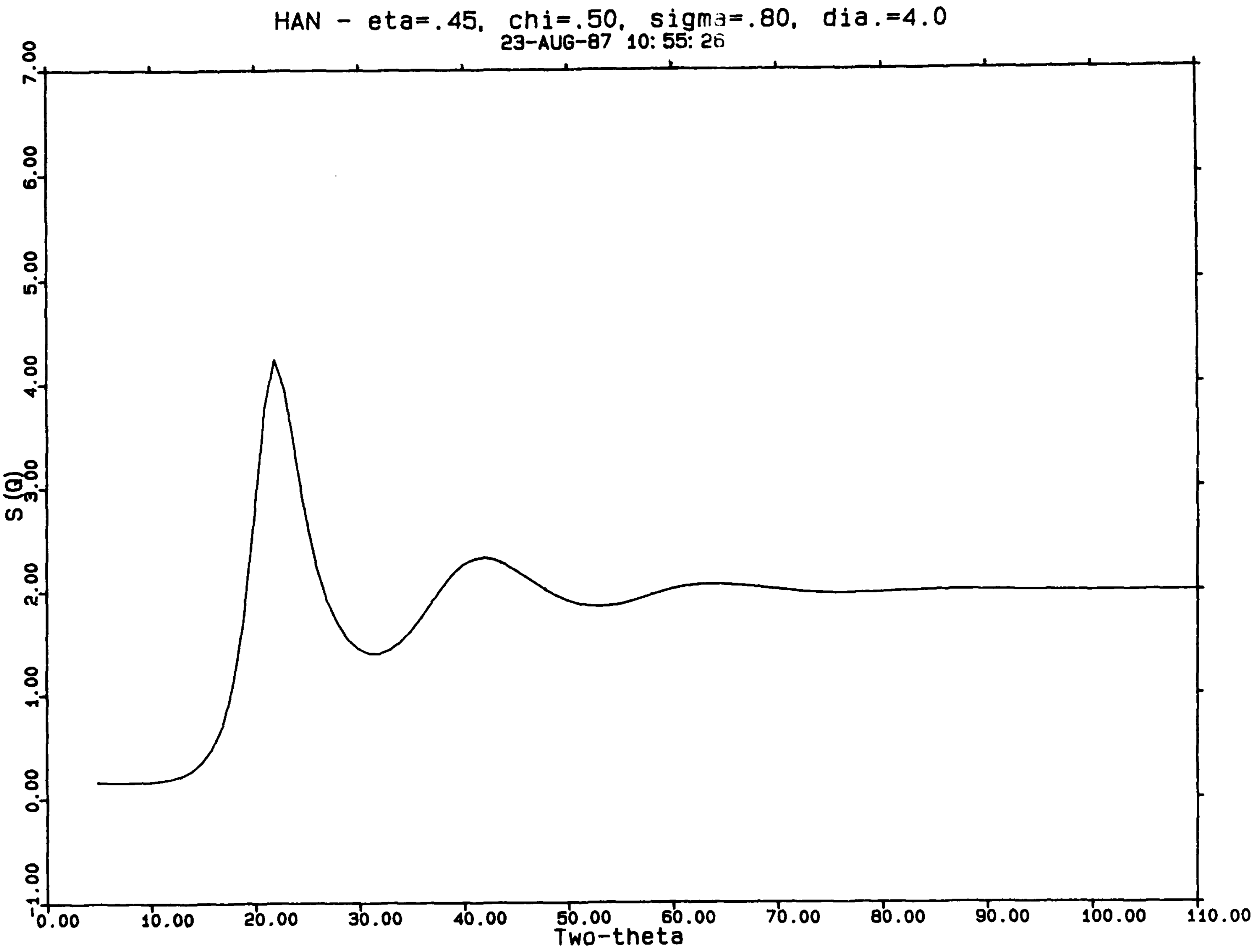
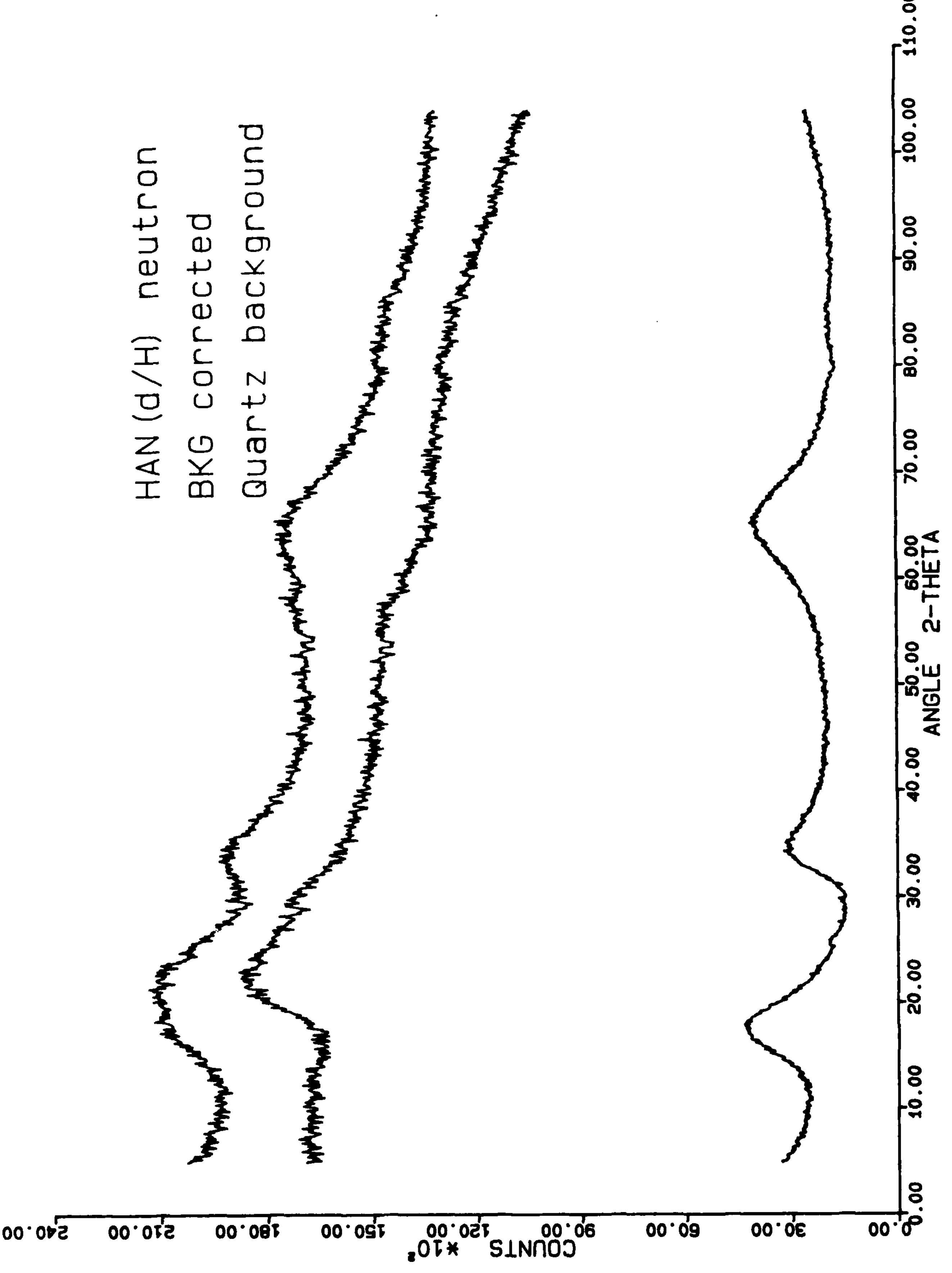
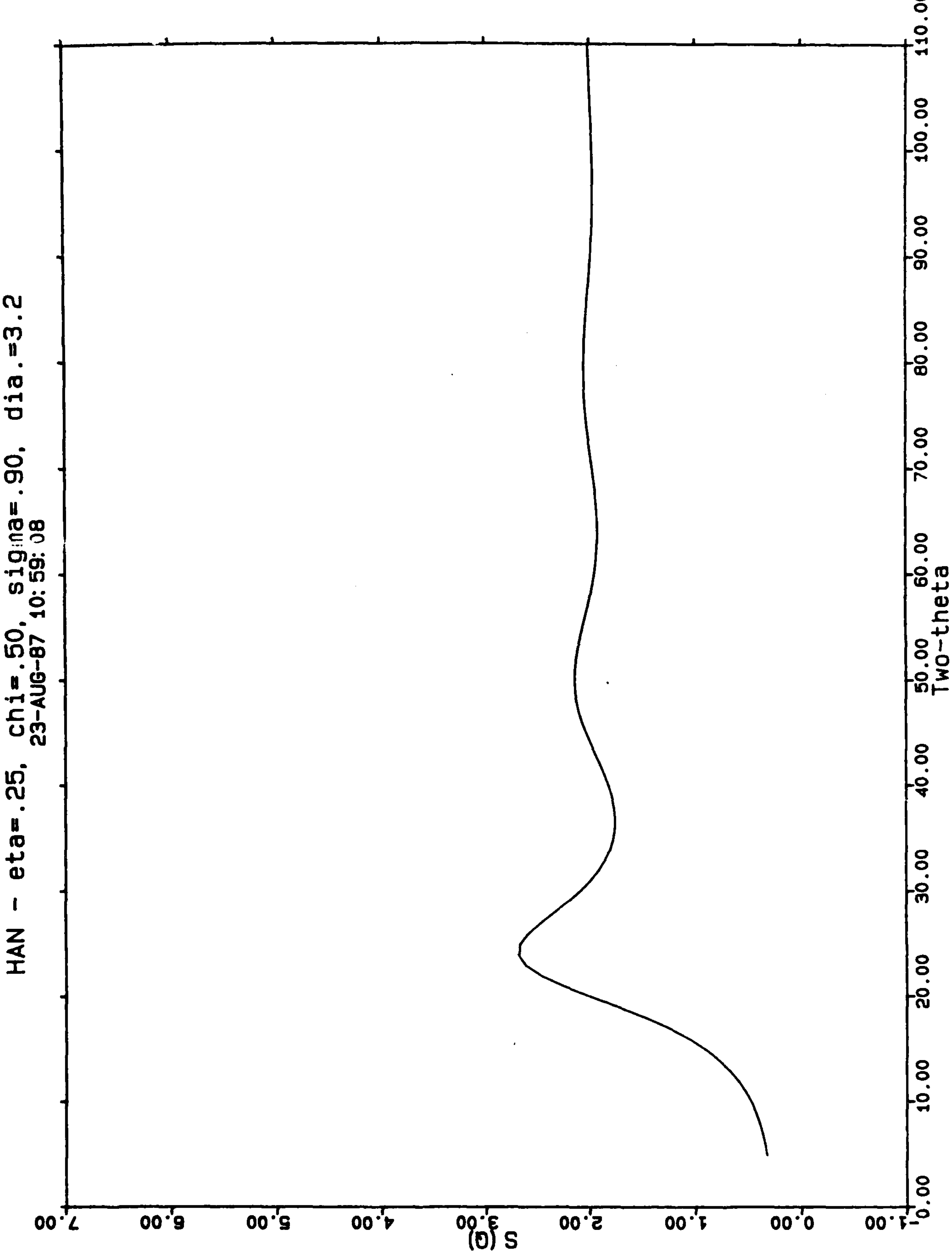
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
ANGLE 2-THETA



HAN - eta=.45, chi=.50, sigma=.80, dia.=4.0
23-AUG-87 10:55:26
S (Q)
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
Two-theta



HAN (d/H) neutron
BKG corrected
Quartz background
ANGLE 2-THETA
COUNTS *10²


HAN - eta=.25, chi=.50, sigma=.90, dia.=3.2
23-AUG-87 10:59:08
S (Q)
Two-theta
-1.00
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2.00
3.00
4.00
5.00
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7.00
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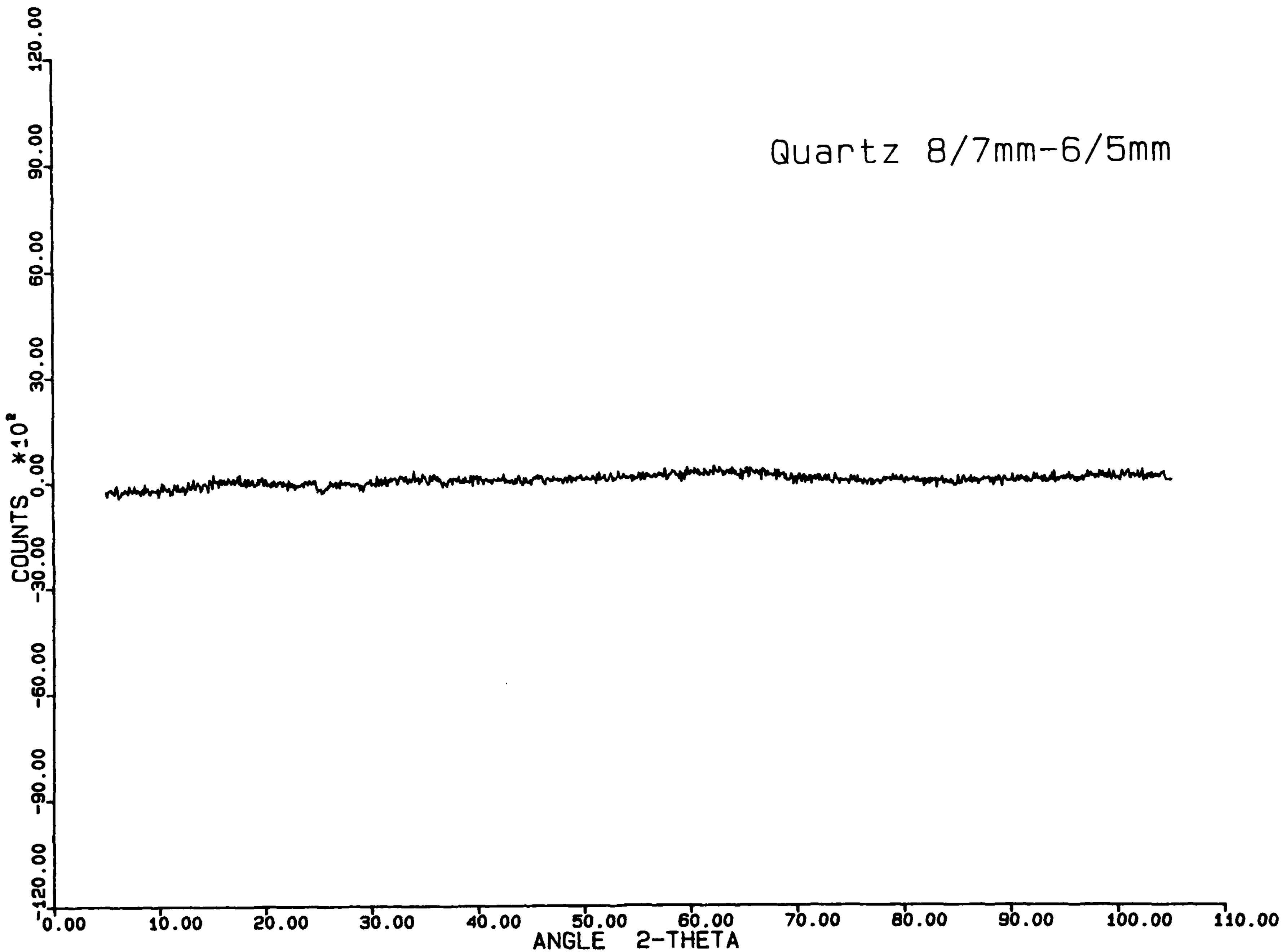


Quartz 8/7mm-6/5mm
COUNTS *10²
120.00
90.00
60.00
30.00
0.00
-30.00
-60.00
-90.00
-120.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
ANGLE 2-THETA

SAMPLE PREPARATION

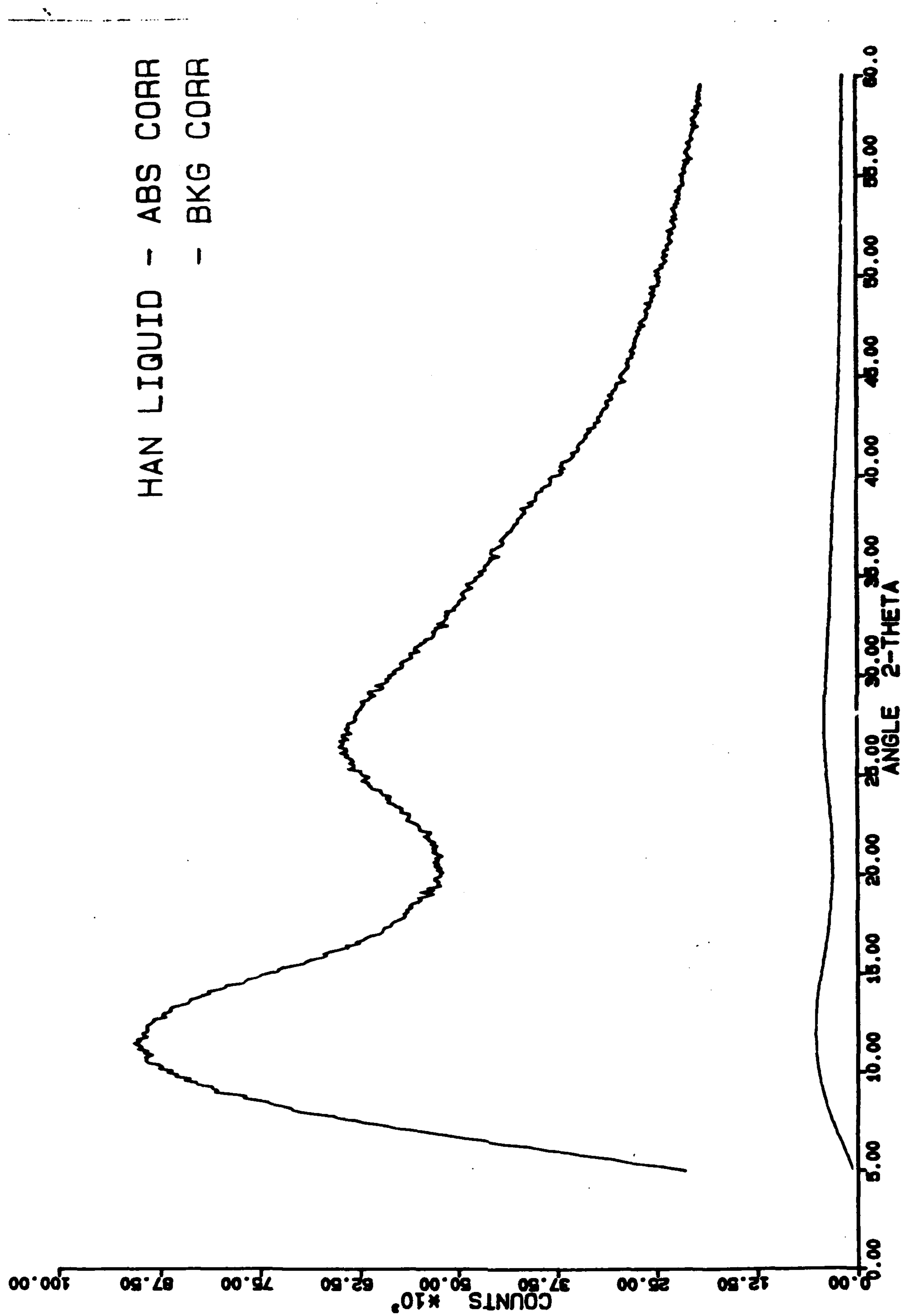
a) Rotary evaporate 18% solution (S. W. Analytical Chemicals) to about 90 weight percent HAN.

b) Vacuum dehydrate at 60-70 degrees C for several hours.

c) Transfer hot liquid (pipet, hypodermic syringe, etc.); use dry atmosphere glove-box if necessary.

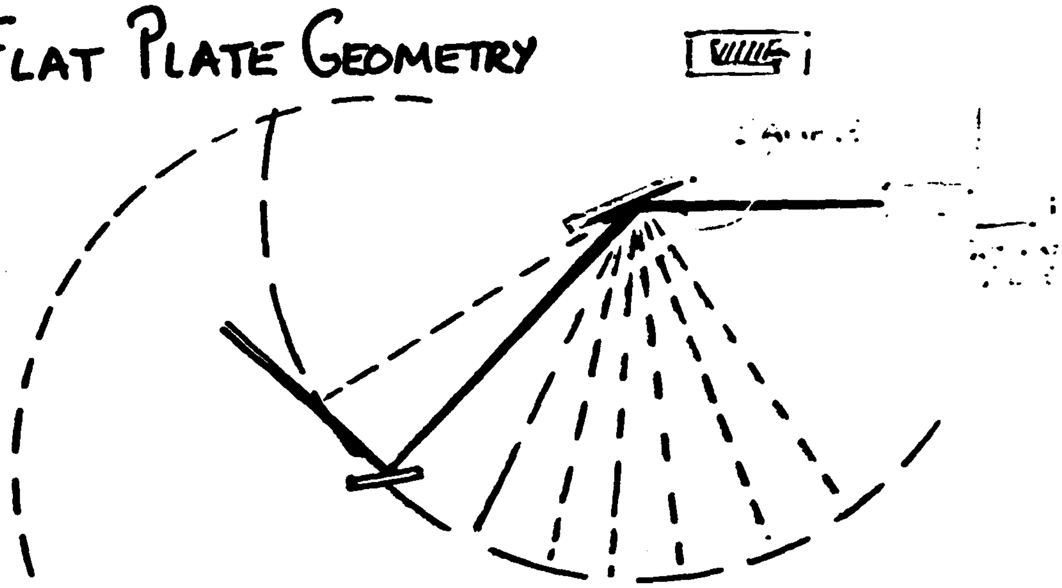
d) Isotopic exchange - dilute dehydrated sample in 99.9% deuterated water (usually for 99.5% exchange in three dilutions).

e) Seal samples in thin-wall quartz tubes or load into polyethylene cell for liquid X-ray scattering.

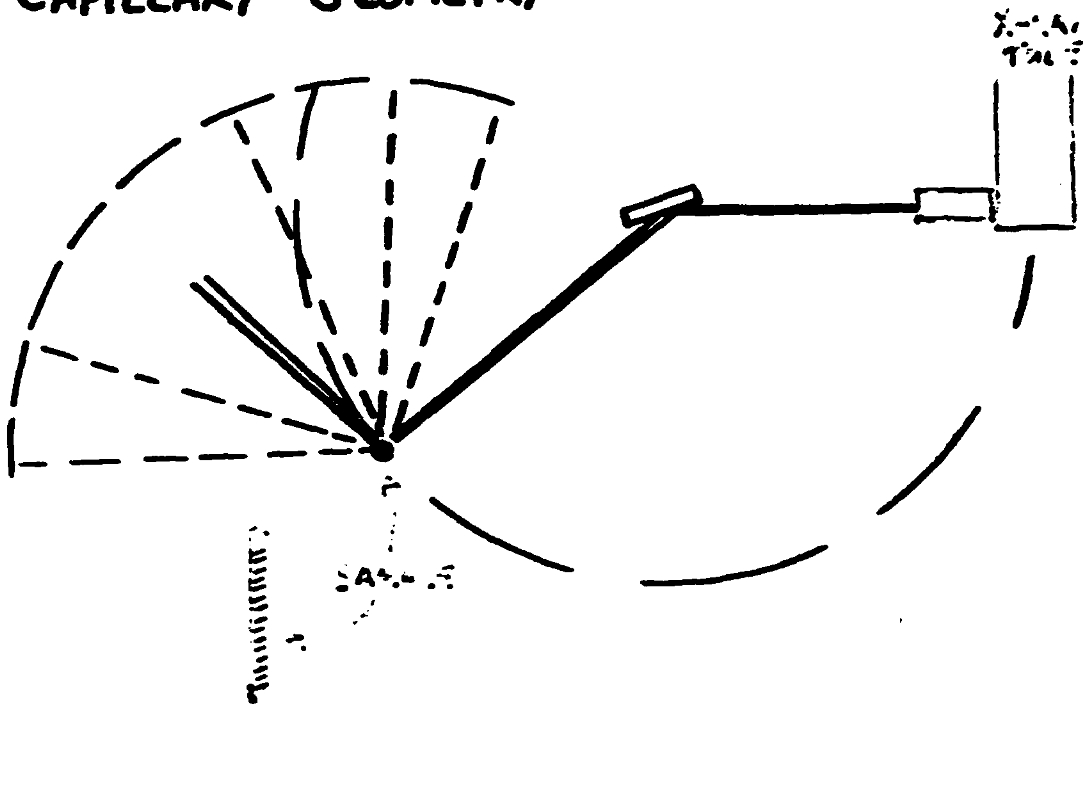


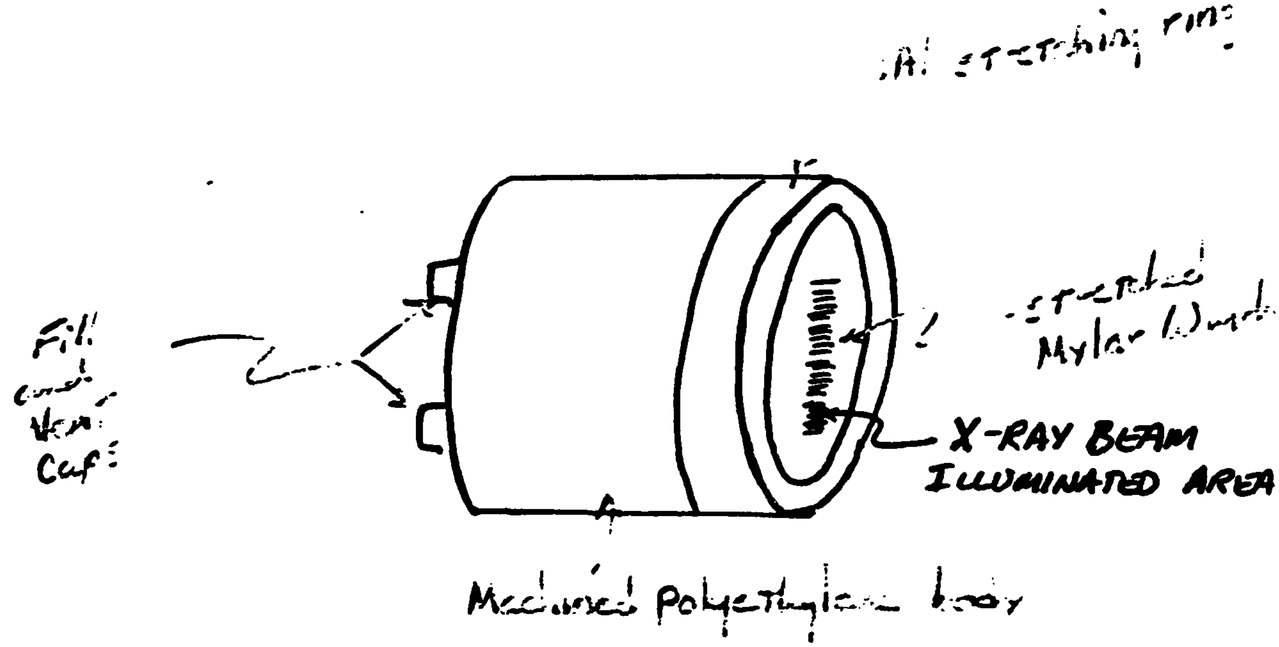
HAN LIQUID - ABS CORR
- BKG CORR
ANGLE 2-THETA
COUNTS *10³
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.0
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00

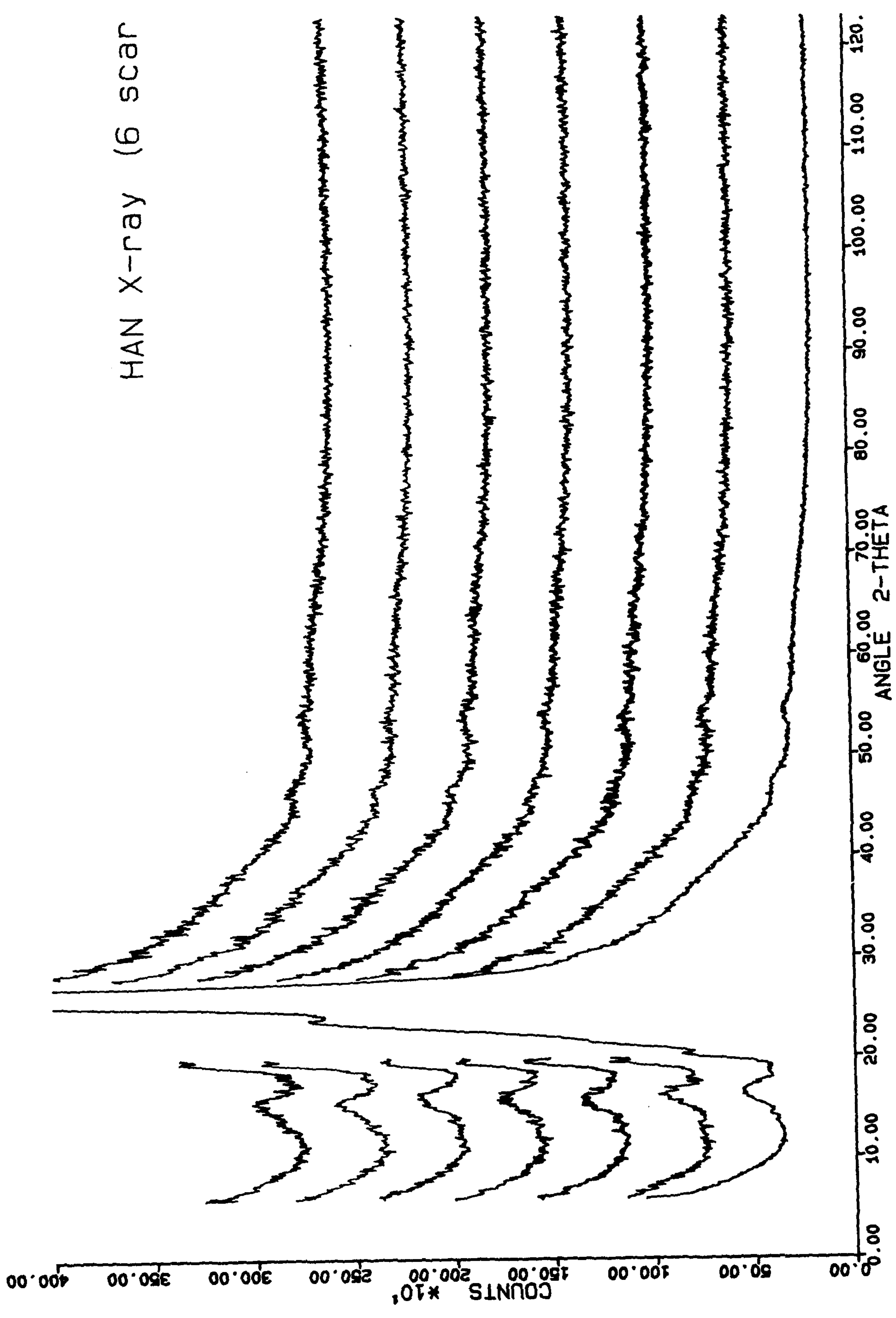
A. Flat Plate Geometry

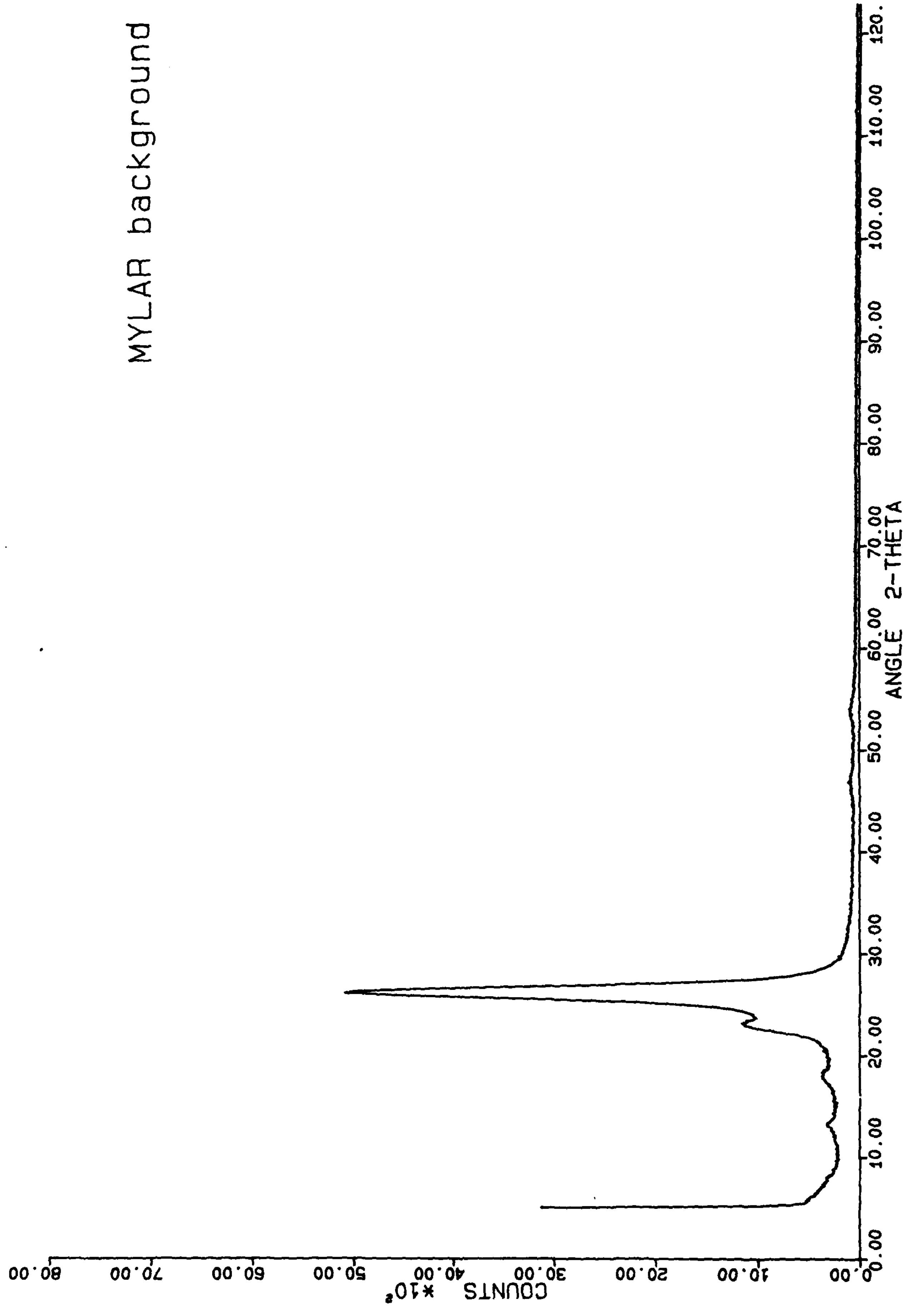


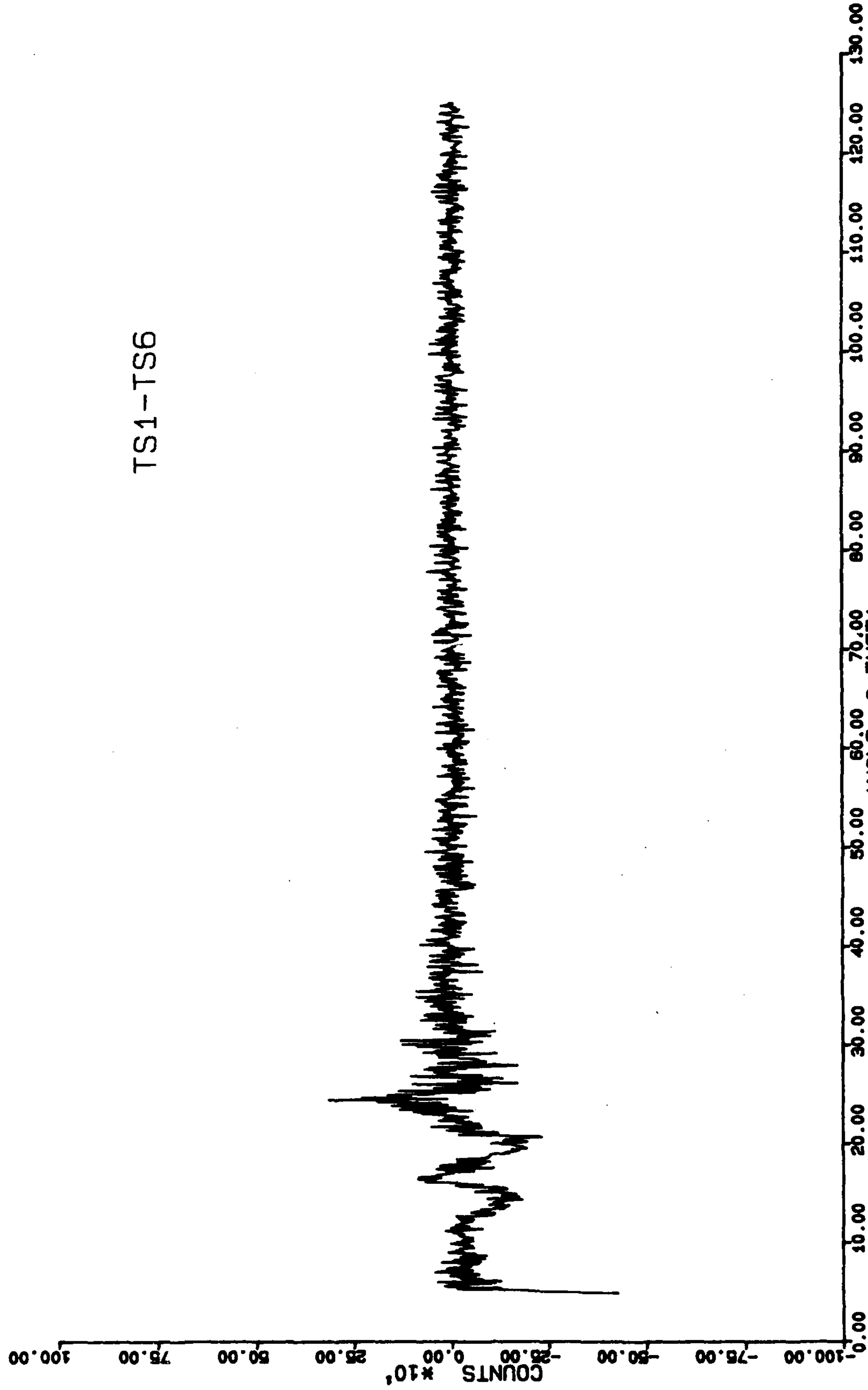
B. Capillary Geometry

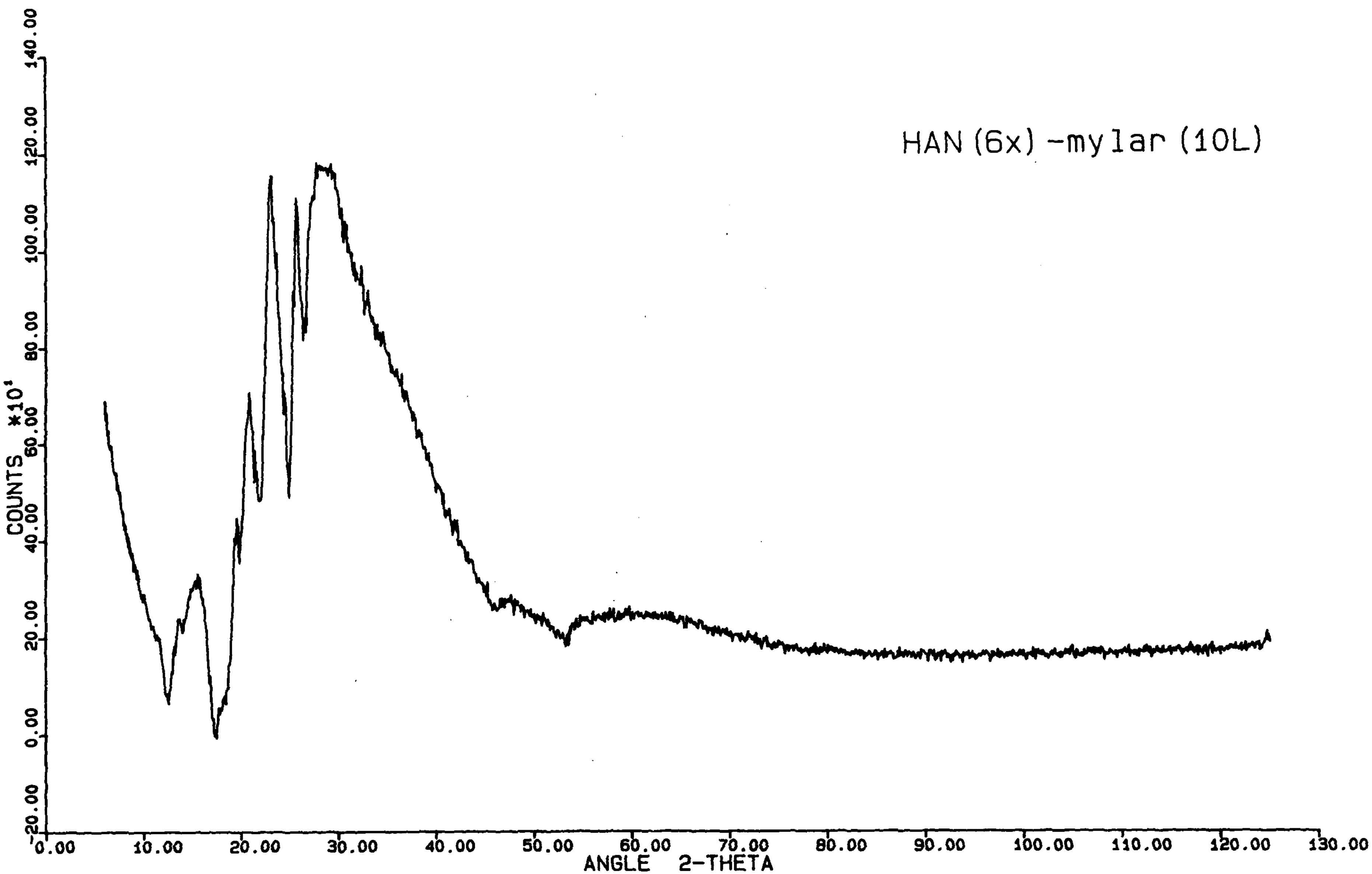



X-RAY BEAM
ILLUMINATED AREA
Machined Polyethylene body


HAN X-ray (6 scar
ANGLE 2-THETA
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.
COUNTS *10¹
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00


MYLAR background
ANGLE 2-THETA
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.
COUNTS *10²
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00


TS1-TS6
ANGLE 2-THETA
COUNTS *10¹
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.00
130.00
-100.00
-75.00
-50.00
-25.00
0.00
25.00
50.00
75.00
100.00


HAN (6x) -mylar (10L)
COUNTS *10¹
ANGLE 2-THETA
-20.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.00
130.00

LIQUID SCATTERING SUMMARY

NEUTRON

1) d4-HAN - better statistics (x2)

2) HAN, Null isotope - x5 to x10 statistics improvement
   incoherent background subtractions
   multiple scattering corrections

X-RAY

1) better liquid cell windows

2) energy sensitive detector (HgI_2)

3) focussing monochromator

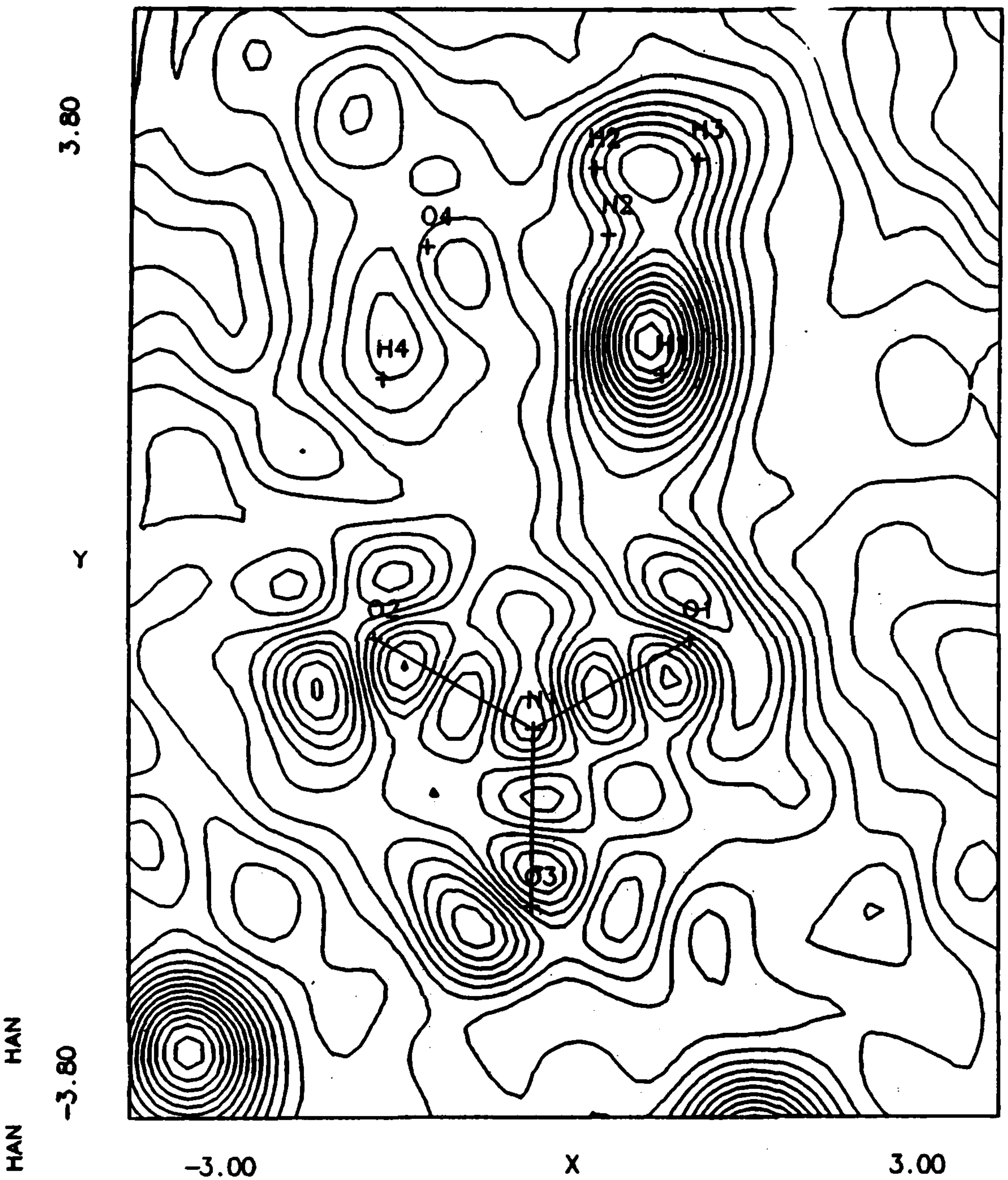
4) shorter wavelengths (smaller window effect)

5) synchrotron experiment

MODELS

1) pursue Percus-Yevick model with non-spherical shape, with form factor, etc.

2) Monte Carlo calculations underway with neutron data
   need better potential for hydroxylammonium ion
   need more crystal structure data (other salts)



NO_3^- X–N

O_1, O_2, O_3 plane

H atoms omitted

Distances from plane

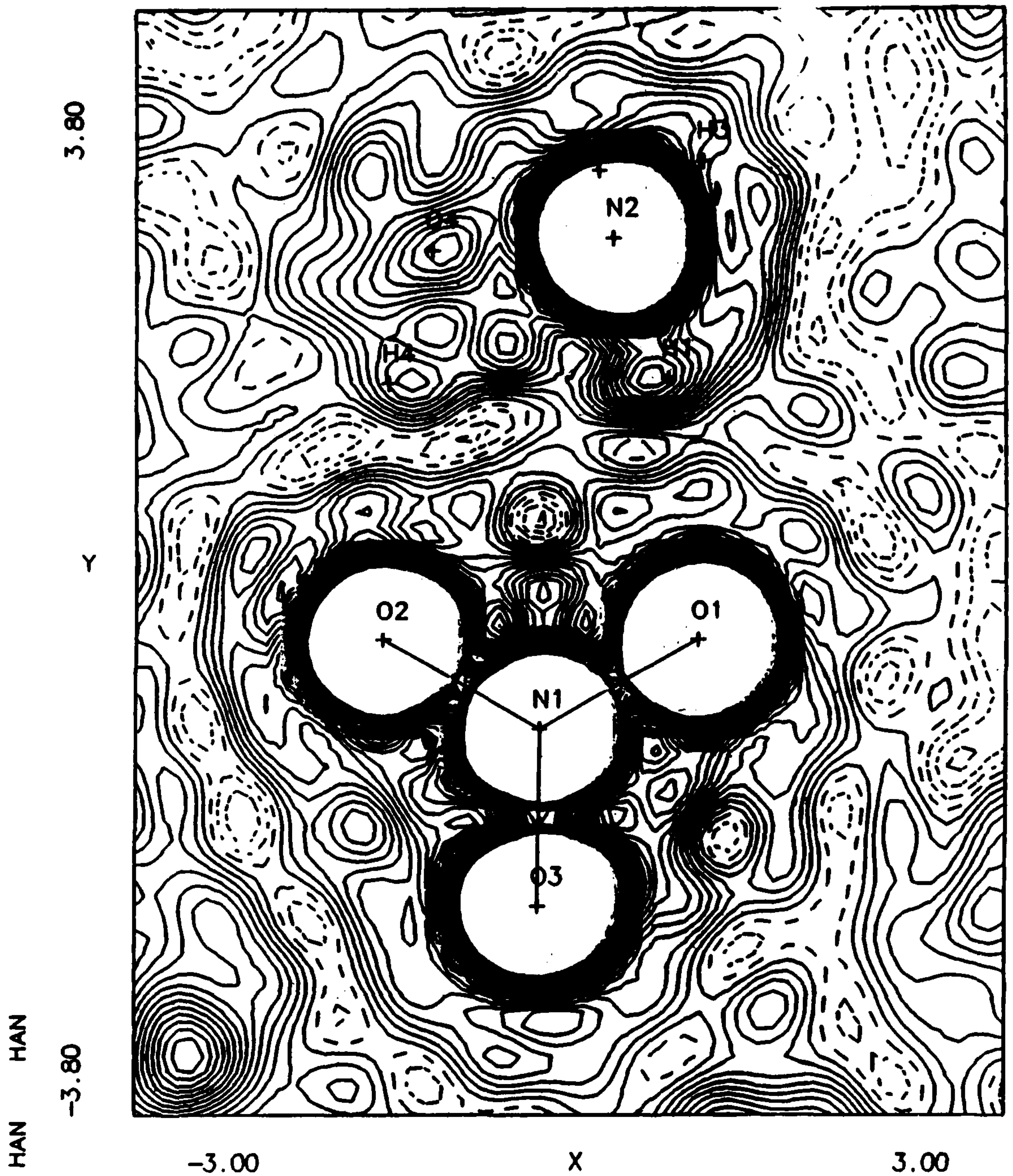
N_1 −.006 Å

N_2 −.051

H1 +.077

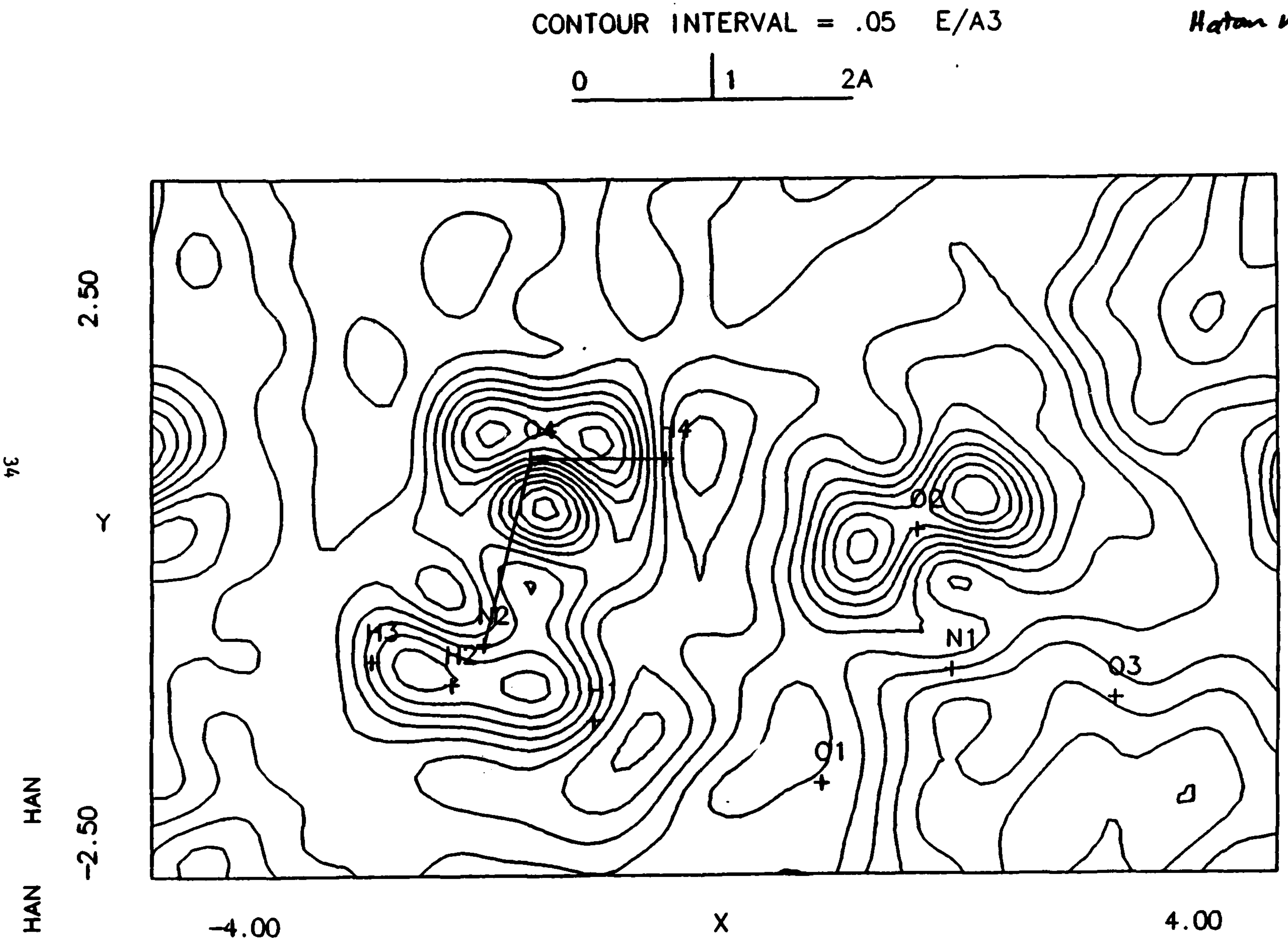
H4 −.50

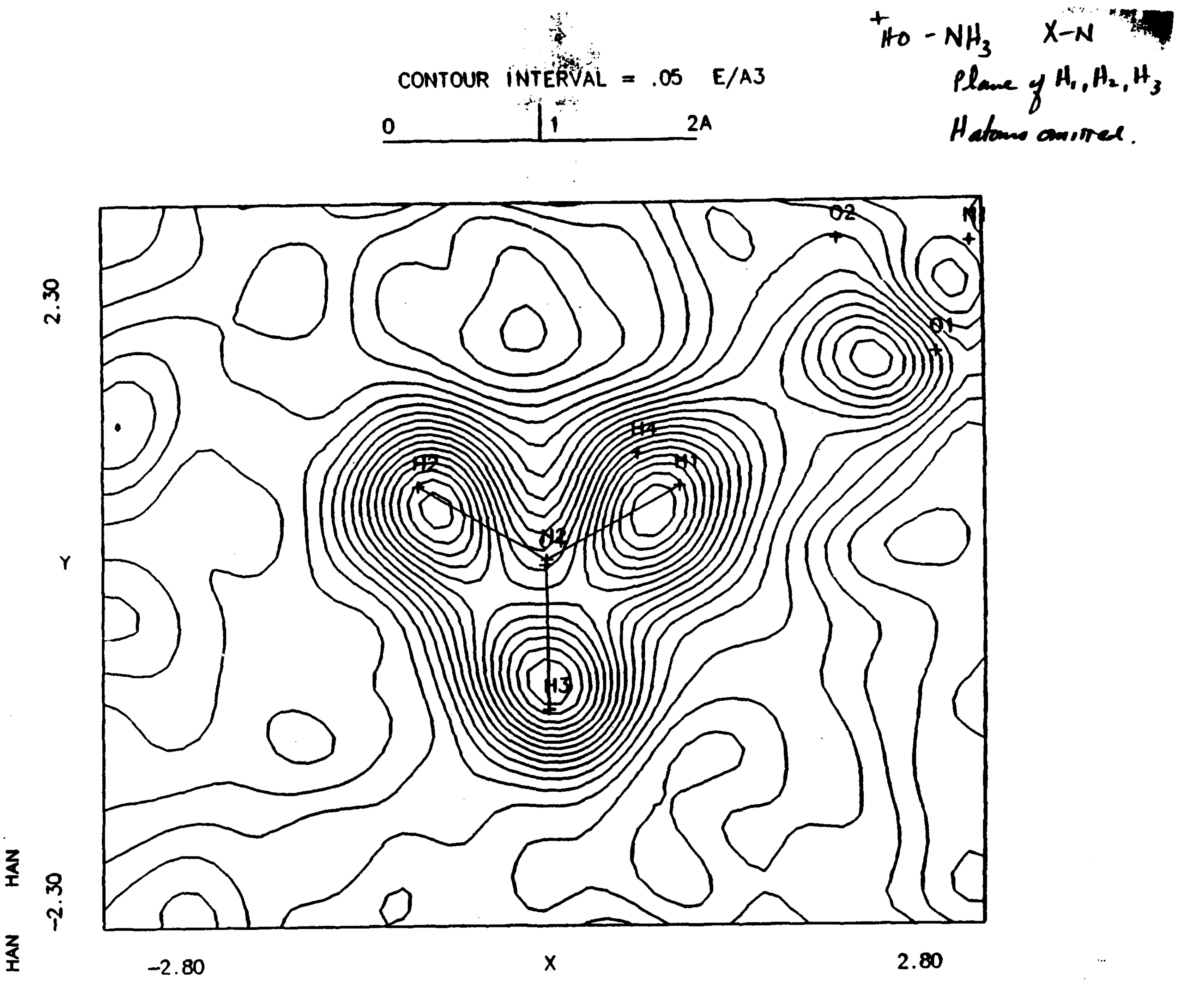
O4 −.68



HAN X-N
Hydrogens included
$0.1\, e^-/\text{Å}^3$ contours
F_{obs}

NH_3-OH^+ X-N
N-O plane
H
H atom included

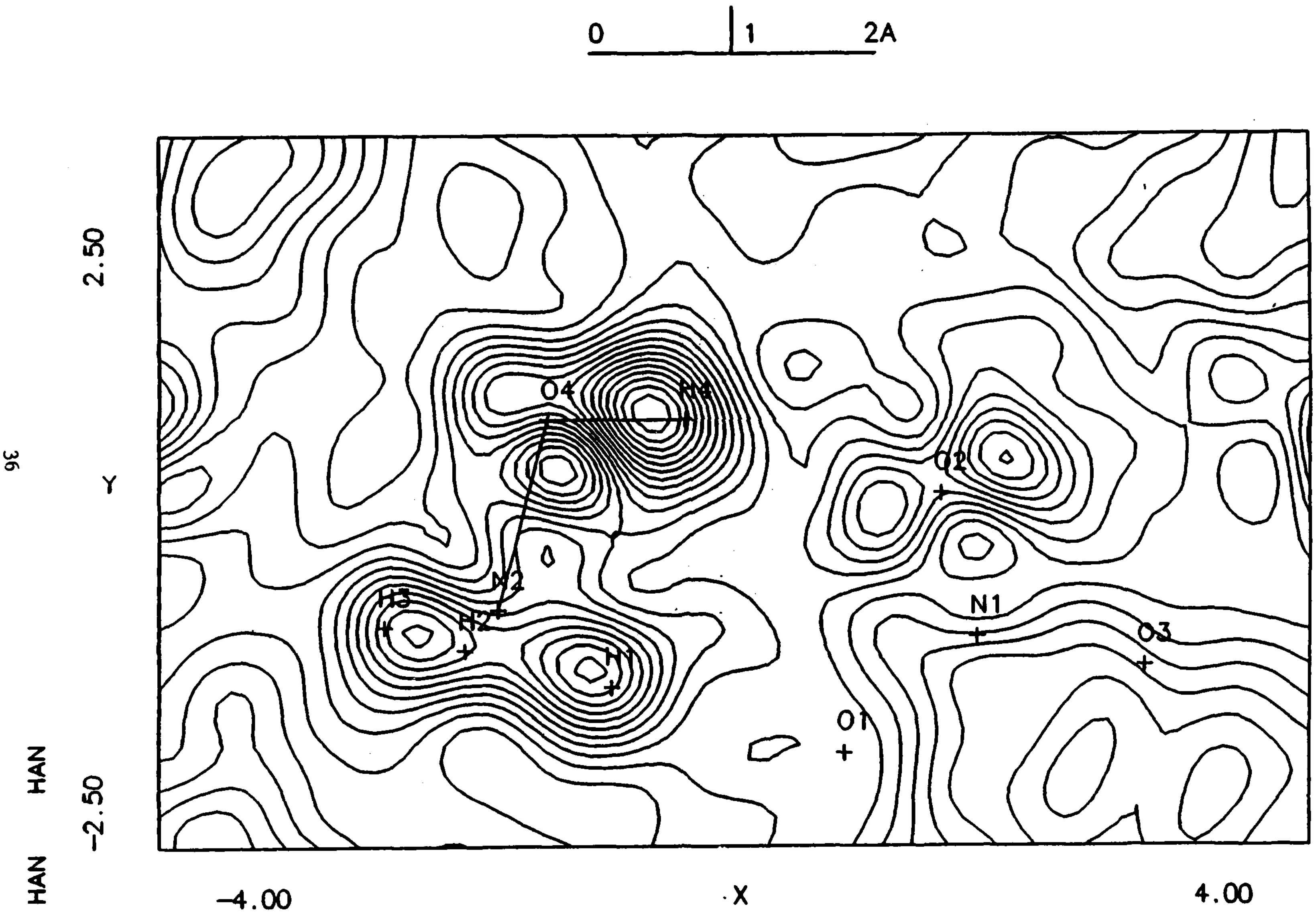




$^{+}Ho-NH_3$ X–N
Plane of H_1, H_2, H_3
H atoms omitted.
CONTOUR INTERVAL = .05 E/A3
0
1
2A
O2
N1
O1
H4
H2
H1
N2
H3
2.30
-2.30
Y
-2.80
X
2.80
HAN
HAN

NH_3OH^+ X–N
N–O_{4+} plane
H atom omitted

CONTOUR INTERVAL = .05 E/A3



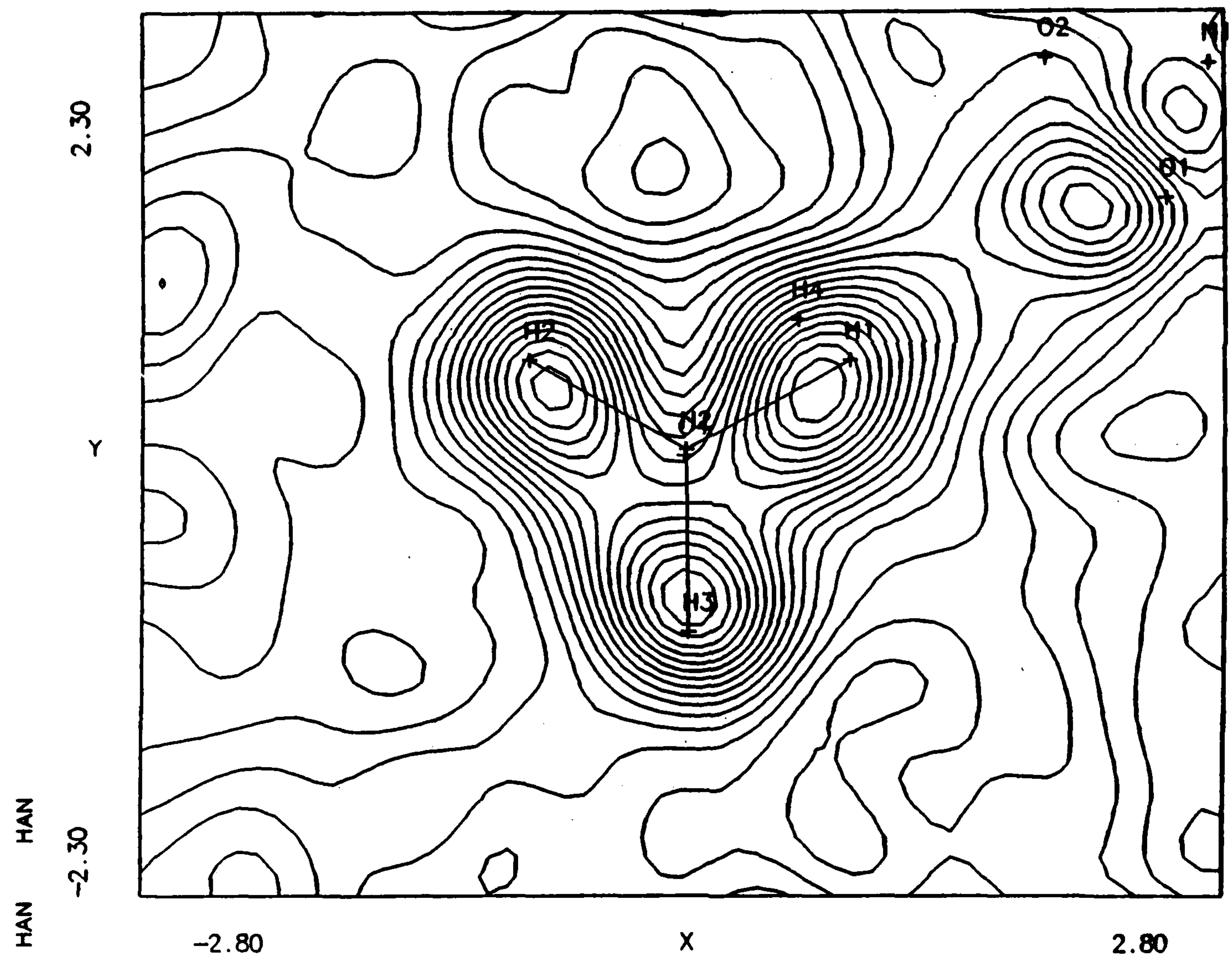
$^{+}HO-NH_3$ X–N

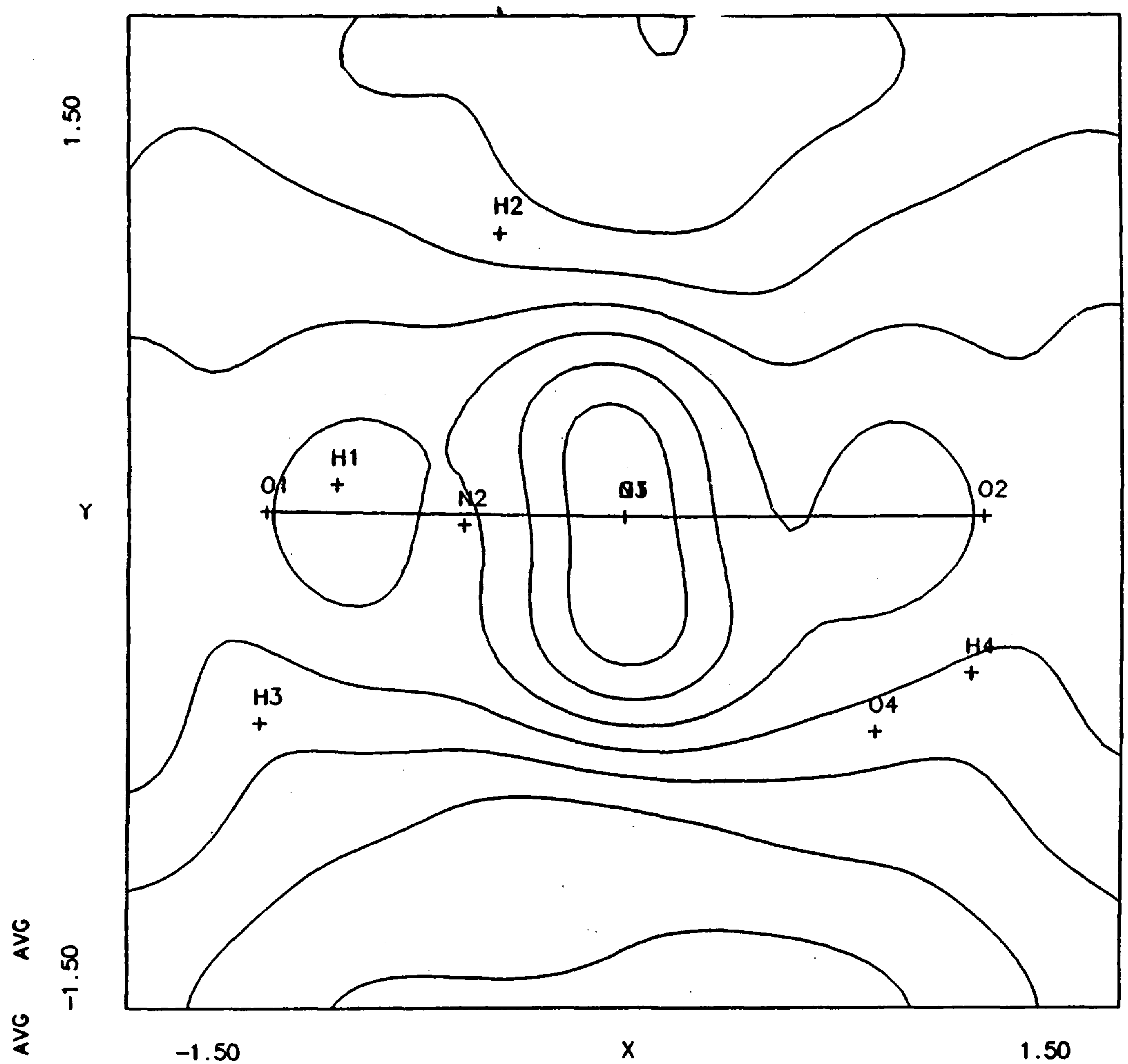
Plane of H_1, H_2, H_3

H atoms omitted.

CONTOUR INTERVAL = .05 E/A3

0 1 2A





NO_3^- X-N
average $\bar{e}$ density
at mid-point of
O_3-N_2 bond.

High Pressure Spectroscopy and the Structure of HAN

Mark A. Davies* and Robert A. Fifer, BRL

Infrared spectra of aqueous solutions of deuterated hydroxylammonium nitrate (dHAN, 11 M in D_2O) have been recorded at pressures ranging from 1 bar to 17.5 kbar. Such data are needed as input and validation for theoretical models used to predict the physical properties of propellants, particularly in the environment of gun barrels at the time of ignition.

Because all protons of HAN are labile, the remaining hydrogen (3%) is distributed between water and the hydroxylammonium ion (DO-H, ND_3OH, HND_2OD). The isolated O-H and N-H vibrations are isotopically uncoupled from O-D and N-D vibrations, eliminating shifting and splitting of vibrational bands due to intramolecular coupling. Correlations between measured O-H bond distances with uncoupled vibrational frequencies allows the distribution of various O-H...O distances, where the O atoms are connected by a hydrogen bond, to be determined.

Pressures were generated using a diamond anvil high pressure cell. The sample was confined between the diamonds using a tantalum gasket. Pressures were measured using the known frequency shift of crystalline quartz as a function of pressure.

The N-O stretch shifts from 991.7 cm^{-1} to 1012.2 cm^{-1} and the nitrate ion bending mode shifts from 825.7 cm^{-1} to 816 cm^{-1}. The intensity of the N-O stretch, greater than that of the 1045 cm^{-1} nitrate ion symmetric stretch at atmospheric pressure, decreases with pressure and is less than that of the 1045 cm^{-1} band at 17.5 kbar. Spectra of the O-H stretching region (above

3000 cm^{-1}) are also shown. Spectral bandwidths of O-H vibrations are much narrower at high pressures. At this time, it has not been determined if a phase change has occurred.

Future studies will include spectroscopic measurements over smaller pressure increments than those used in these preliminary experiments, as well as concentration and temperature dependence studies at high pressures. In addition, it is hoped that the HAN band positions at various pressures can be calibrated against the crystalline quartz standard, eventually eliminating the need for the addition of the pressure standard to the sample.

* National Research Council Postdoctoral Associate

Isotopic Uncoupling Spectroscopy

<u>uncoupled vibration</u>	<u>species measured</u>
HO—H	DO—H in dHAN
$H_3\overset{+}{N}O—H$	$D_3\overset{+}{N}O—H$ in dHAN
$HO\overset{+}{N}H_2—H$	$DO\overset{+}{N}D_2—H$ in dHAN

where $dHAN \equiv D_3\overset{+}{N}OD + NO_3^- + D_2O$
(97% D, 3% H)

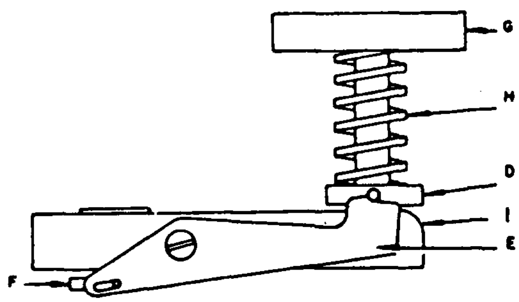
ADVANTAGES OF FTIR

speed of data aquisition
lack of sample fluorescence
lack of diamond fluorescence

DIAMOND ANVIL CELL ADVANTAGES

simplicity of operation
small sample volumes

Figure 2. Diamond anvil optical cell. Cross-section of cell: A, Diamonds; B, piston (composed of two parts held together by screws which provide for relative movement of the two parts for alignment purposes); C, hardened steel cylinder; D and F, two presser plates connected by the lever arms, E; G, screw; H, calibrated spring; I, steel body.



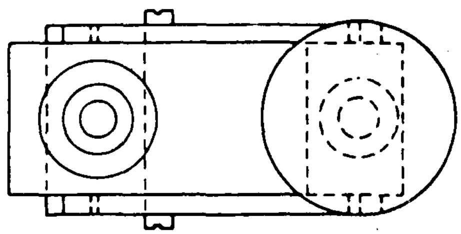
SIDE VIEW

Length: 12.0 cm.

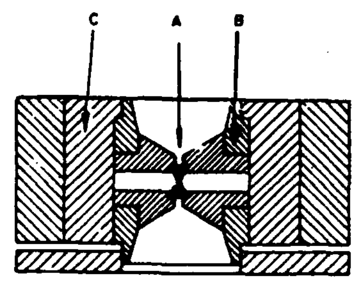
Base Height: 2.5 cm.

Width: 7.5 cm.

Spring Height: 3.5 cm.



TOP VIEW



DETAIL OF DIAMOND CELL

PROBLEMS

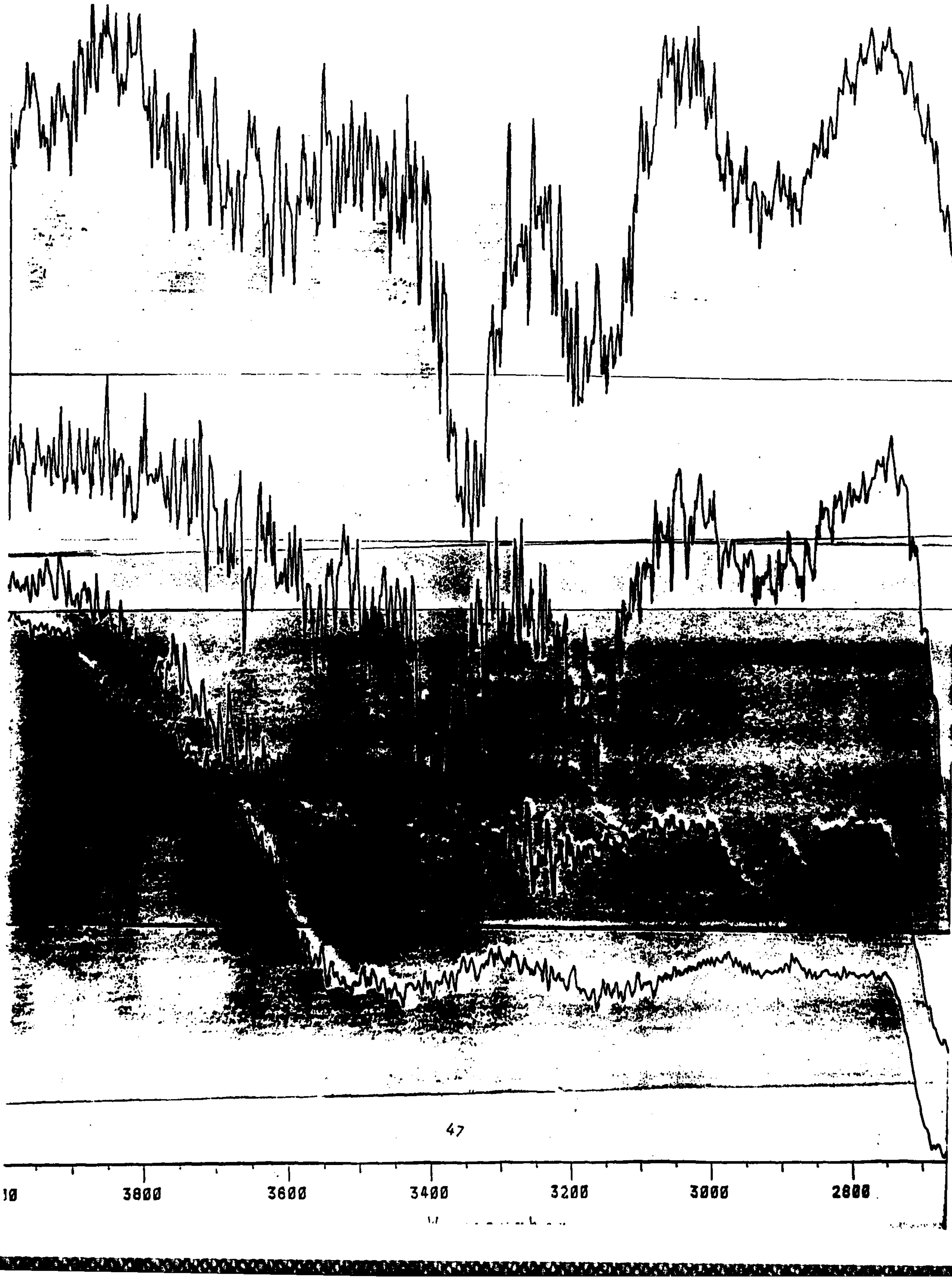
1. absorption strength necessitates very short path lengths
   a) difficulty in making gaskets
   b) pressure standard (ruby or quartz) must be ground to very small size

2. light throughput is small due to small gasket aperture size

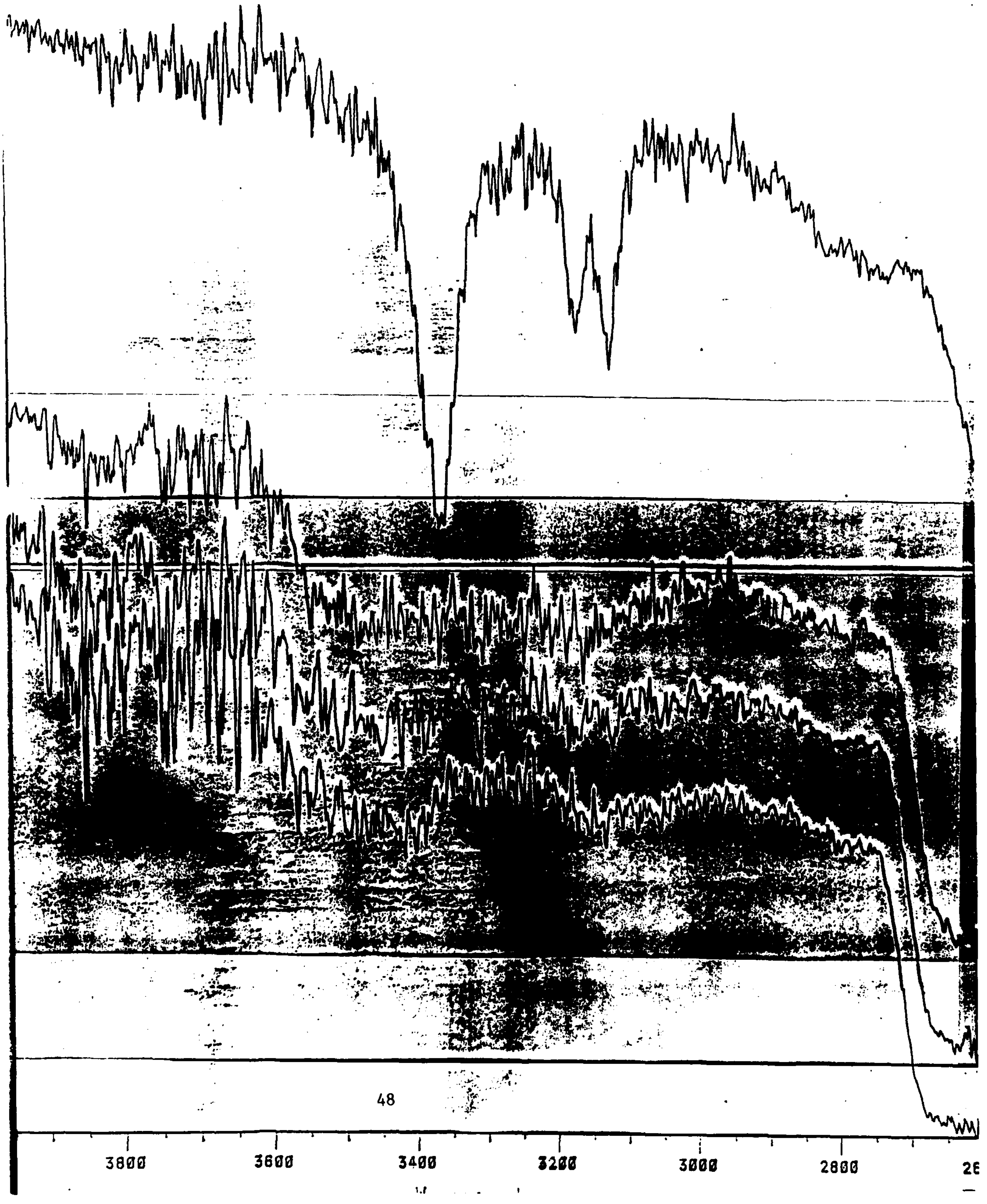
EXPERIMENTAL

Mattson Sirius 100 FTIR w/ beam condensing optics
DAC by High Pressure Diamond Optics Inc., Tucson, AZ
4 cm^{-1} resolution
400 scans per spectrum
Tantalum gaskets, 0.4mm - 0.5 mm diameter
20 micron pathlength (before pressurization)
Pressures were calibrated against a crystalline quartz standard
(Wong, Moffatt, Baudais, Appl. Spectrosc. 39, 4, 733, 1985)

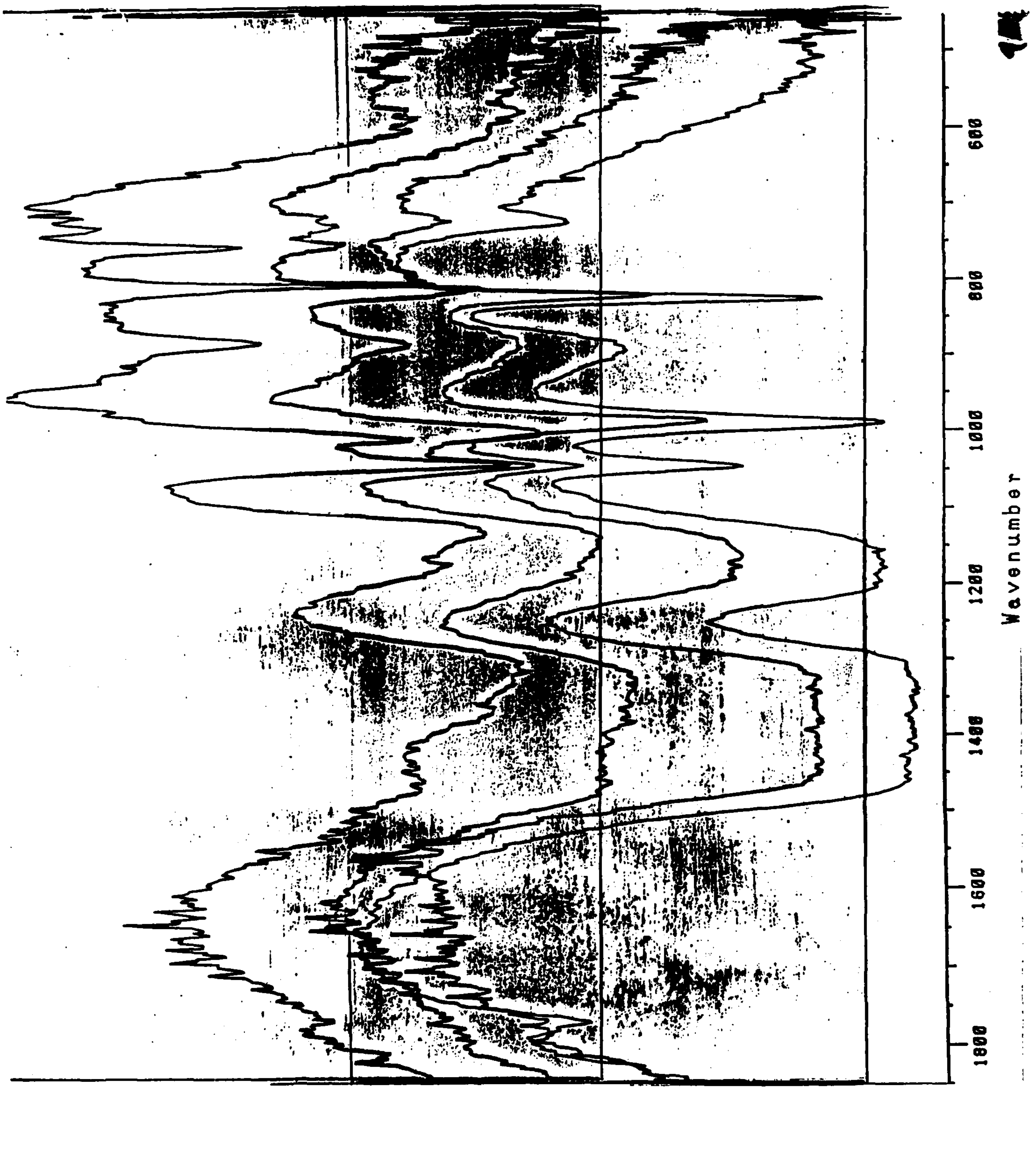
Calibration was carried out externally using a gasket of the same thickness as that used in the experiment. KBr transmitted the pressure.

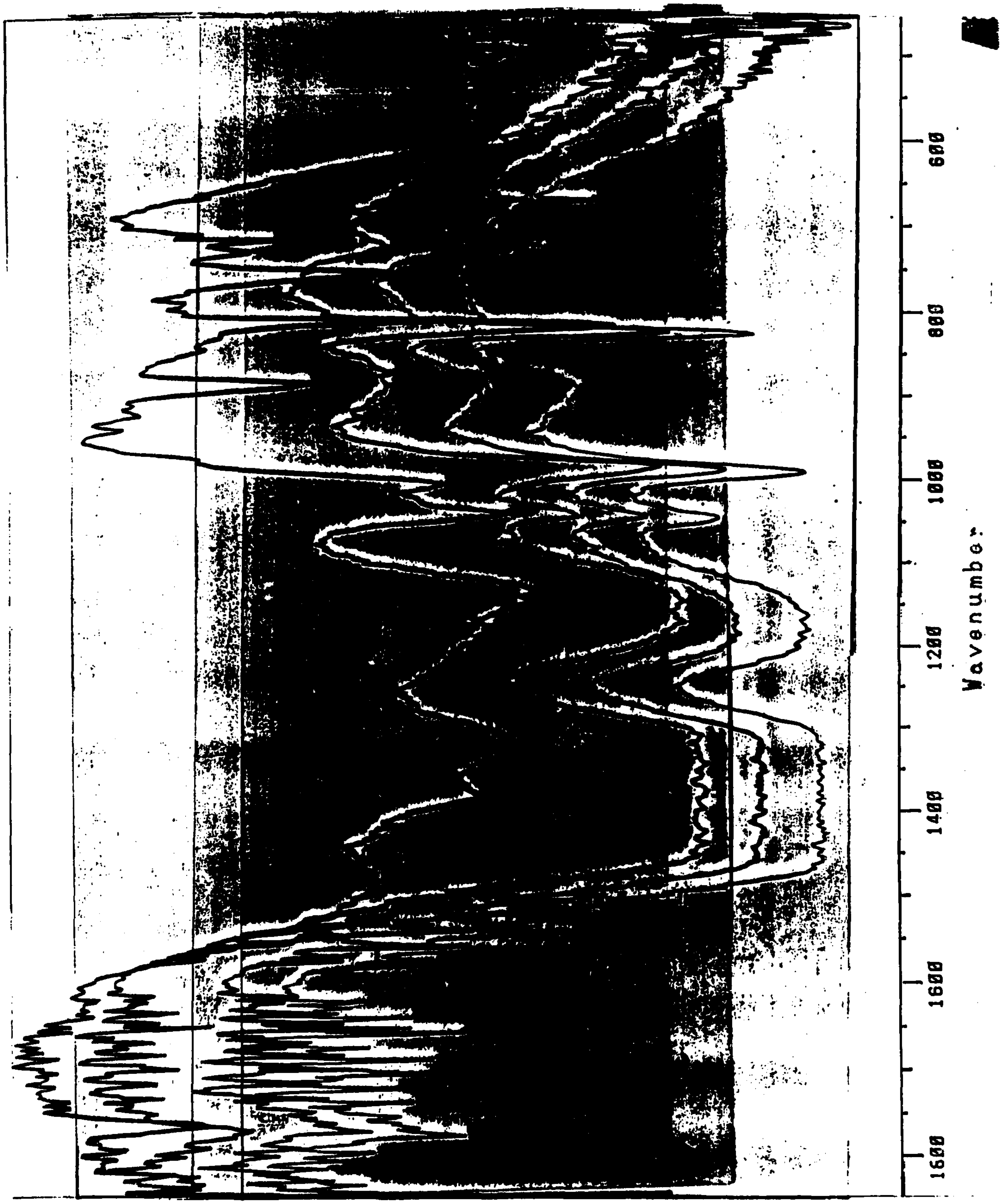


3800
3600
3400
3200
3000
2800



3800
3600
3400
3200
3000
2800


600
800
1000
1200
1400
1600
1800
Wavenumber


600
800
1000
1200
1400
1600
Wavenumber

FUTURE WORK

calibrate pressure sensitive HAN lines against quartz or ruby
(make HAN into its own pressure gauge)
use smaller pressure increments & determine onset of decomposition
concentration & temperature effects

ACKNOWLEDGMENTS

R. Fifer
N. Klein
L. Decker
M. Decker
R. Sassé
Prof. P. Garn

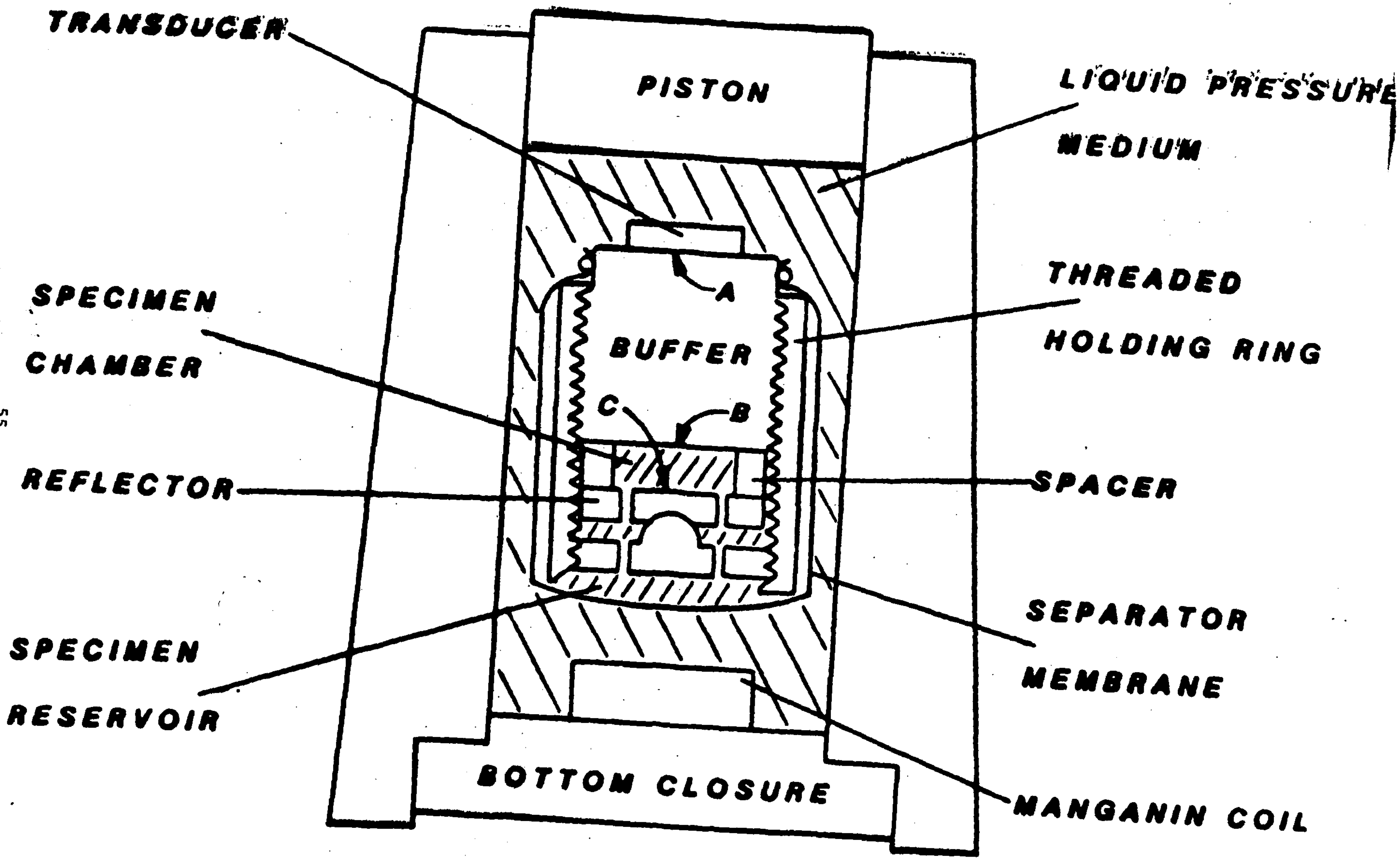
National Research Council

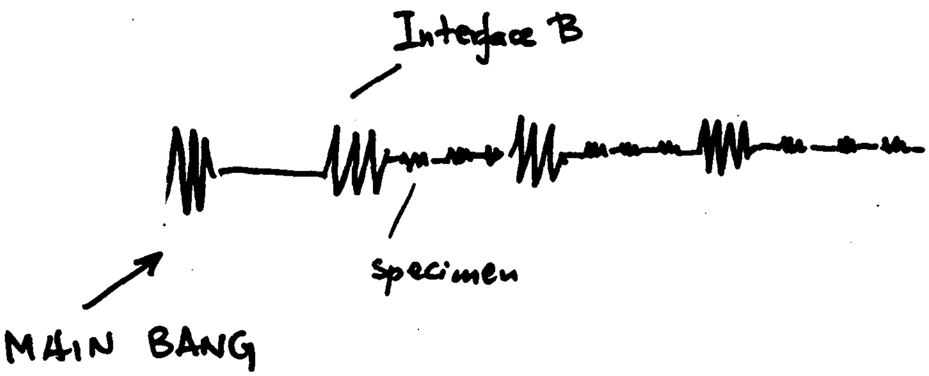
RAMAN SPECTROSCOPY OF AQUEOUS SOLUTIONS AT HIGH TEMPERATURES AND PRESSURES. P. D. Spohn and T. B. Brill, University of Delaware, Newark, De 19716.

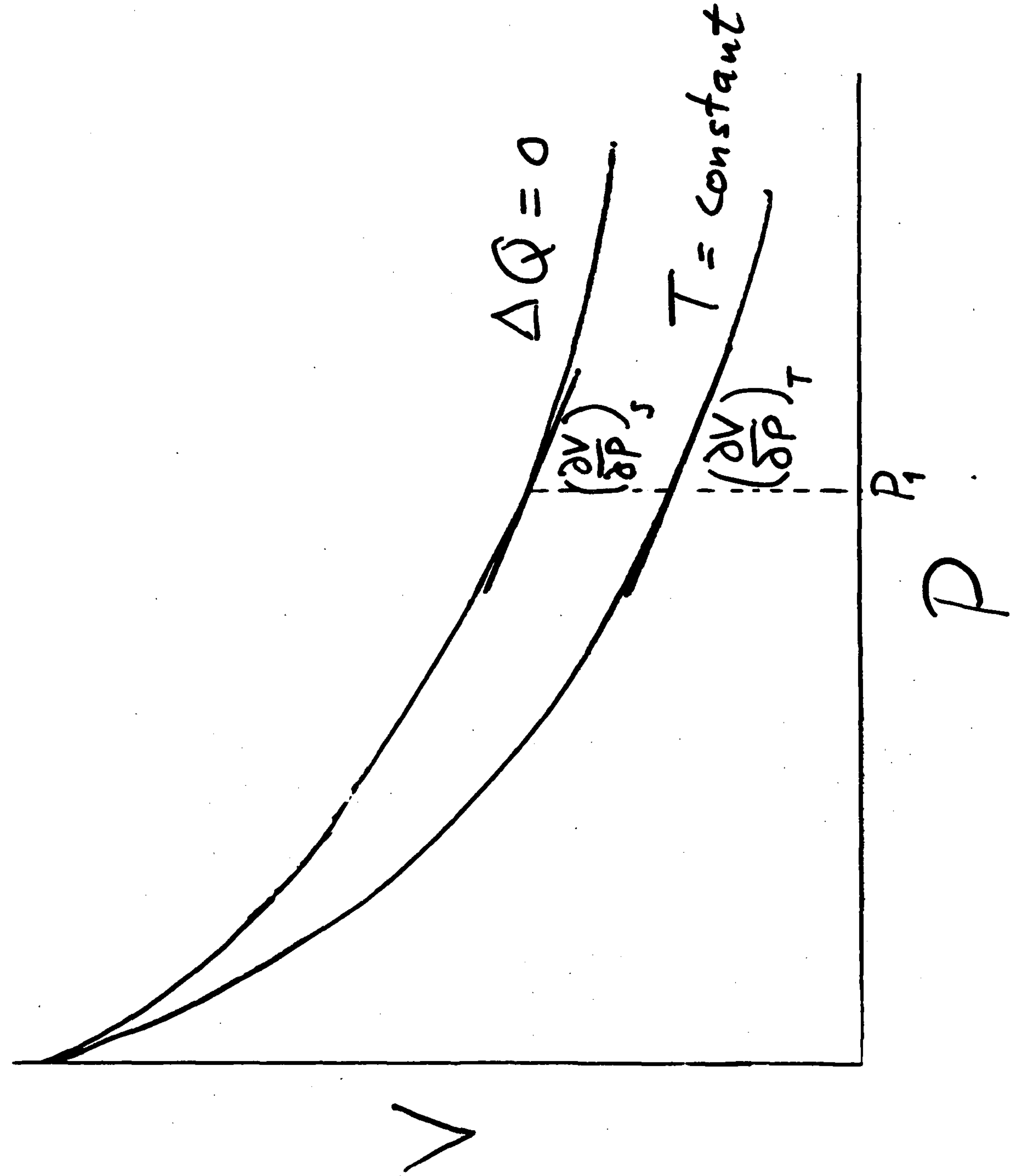
Raman spectroscopy has been shown to provide information on the microscopic organization of the aqueous nitrate ion. Previous studies have been limited to lower temperatures due to the corrosivity that is inherent in these systems. The development of a cell capable of containing corrosive salts under exteme conditions (450° C, 5000 psi) will be described. The study of aqueous inorganic nitrate salts under these conditions will be presented. The possibility of elucidating microscopic structures for metal-nitrate salts and metal-nitrate-HAN mixtures from these studies will be examined.

THE HIGH PRESSURE SOUND VELOCITY, EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF AGUEOUS MIXTURES OF HAN AND TEAN

J. FRANKEL & M. DOXBECK


TRANSDUCER
PISTON
LIQUID PRESSURE MEDIUM
SPECIMEN CHAMBER
A
BUFFER
THREADED HOLDING RING
C
B
REFLECTOR
SPACER
SEPARATOR MEMBRANE
SPECIMEN RESERVOIR
BOTTOM CLOSURE
MANGANIN COIL


Interface B
specimen
MAIN BANG



ΔQ = 0
T = constant
$\left(\frac{\partial V}{\partial P}\right)_S$
$\left(\frac{\partial V}{\partial P}\right)_T$
P_1
P
V

THE SOUND VELOCITY MEASURES AN

ADIABATIC PROPERTY :

$$\frac{1}{K_s} = \rho v^2$$

where $K_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s$ and $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

on an isothermal curve

BUT WE CAN RELATE THEM

$$K_T = K_s + \frac{TV\beta^2}{C_p}$$

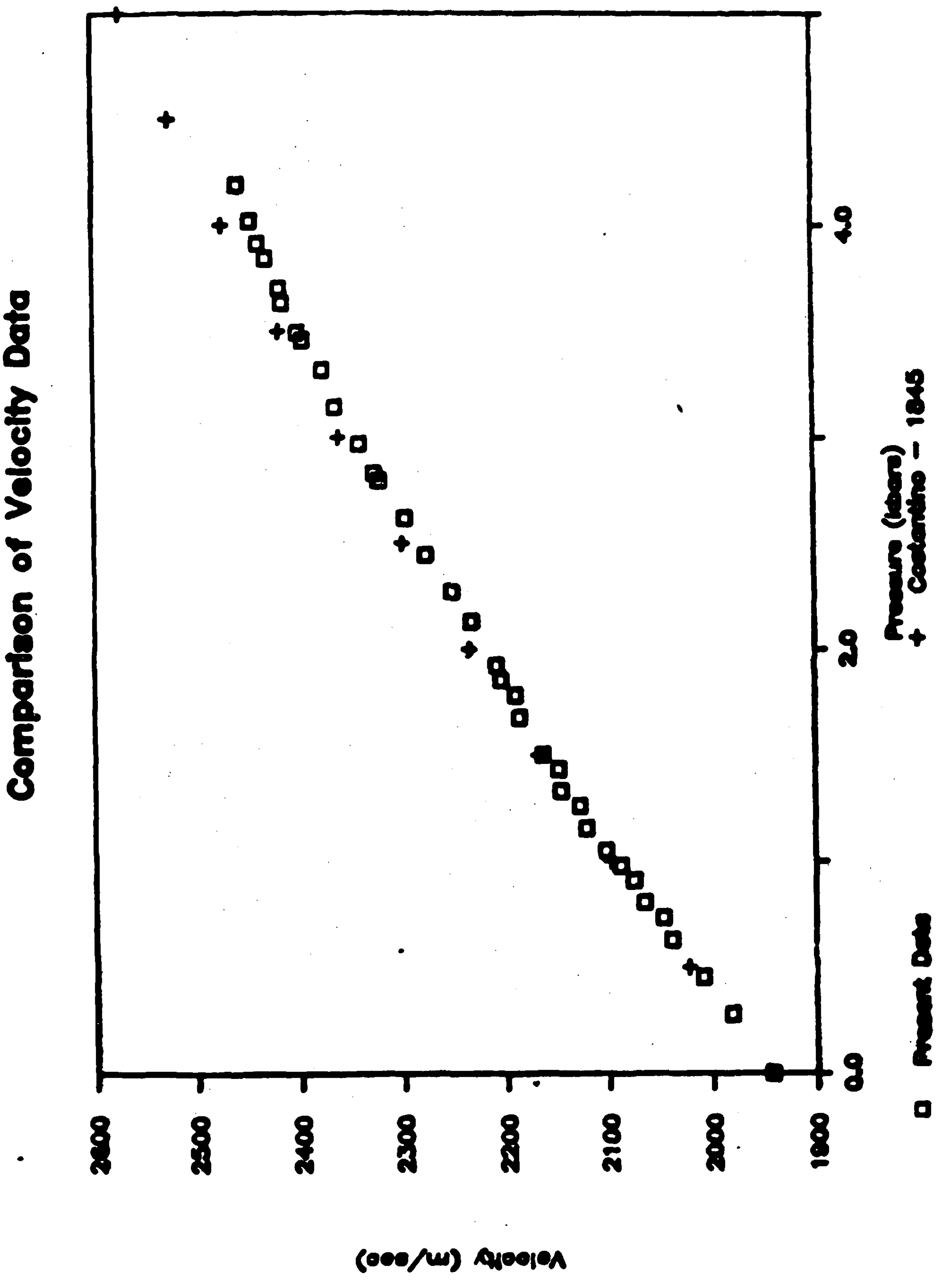
HENCE $\left.\frac{\partial V}{\partial P}\right)_T = -\frac{TV\beta^2}{C_p} - \frac{V^2}{v^2}$

AND FINALLY:

$$\rho(P) - \rho(P_0) = \int_{P_0}^{P} \frac{dP}{v^2} + \int_{P_0}^{P} \frac{T\beta^2}{C_p} dP$$

from Maxwell relations the Pressure dependence

is found $\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial K_T}{\partial T}\right)$; $\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$



Comparison of Velocity Data
Velocity (m/sec)
2600
2500
2400
2300
2200
2100
2000
1900
0.0
2.0
4.0
Pressure (kbars)
□ Present Data
+ Costantino – 1945

Comparison of Change In Density Data

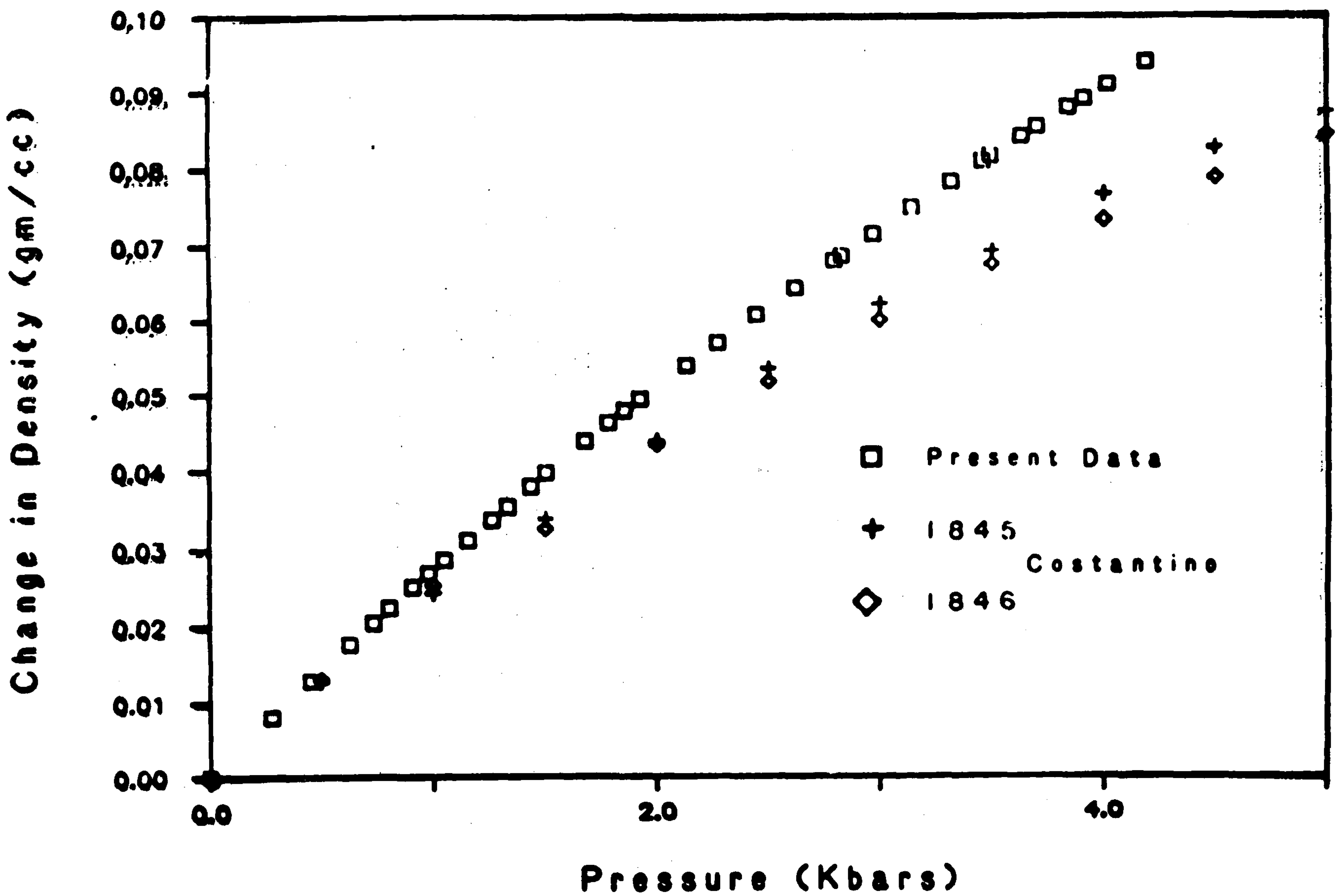
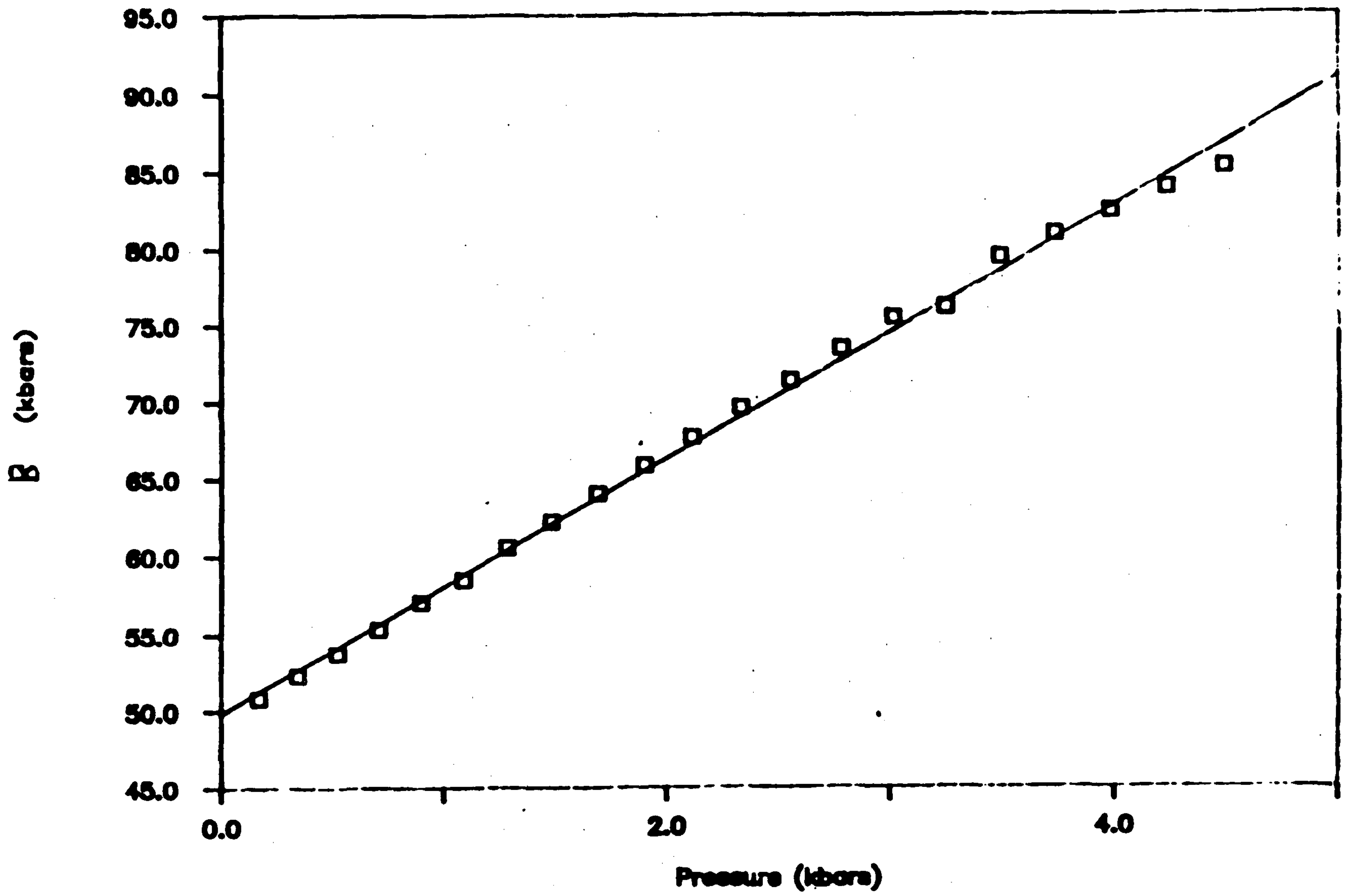


TABLE 2. Pressure and Temperature Dependence of Thermodynamic Quantities* (Obtained Here)

Equation	Units
$v(T) = 1966 - 1.703T$	m/sec, °C
$K_T(T) = 1.954\times10^{-5} + 5.200\times10^{-8}T$	bar^{-1}, °C
$v(P) = 1942.79 + 0.154P - 6.482\times10^{-6}P^2 - 1.638\times10^{-10}P^3$	m/sec, bar
$\rho(P) = 1.4532 + 2.9387\times10^{-5}P - 2.1711\times10^{-9}P^2 + 1.2192\times10^{-13}P^3$	gm/cm^3, bar
$B(P) = 48679 + 10.848P$ (Tait Equation)	bar, bar
$C_p(P) = 2.29 + 9.78\times10^{-6}P$	joules/ gm K, bar
$\beta(P) = 4.898\times10^{-4} - 5.20\times10^{-8}P$	K^{-1}, bar
$K_T(P) = 2.02\times10^{-5} - 3.38\times10^{-9}P + 3.36\times10^{-13}P^2$	bar^{-1}, bar

*Pressure dependence found at room temperature (23°C). Temperature dependence found at one atmosphere.

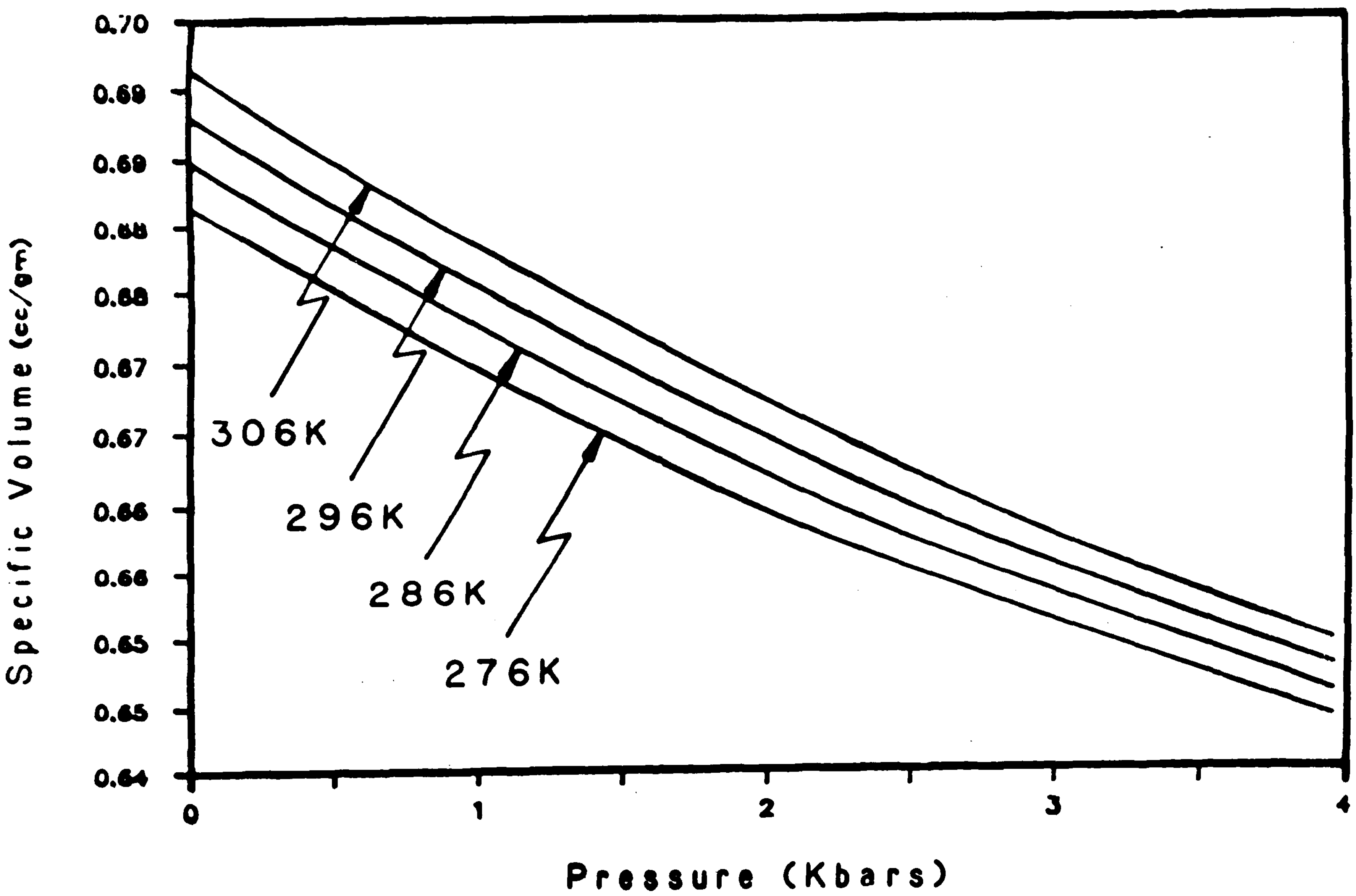
Tait Equation



TO OBTAIN THE TEMPERATURE DEPENDENCE FOR PHASE REGIONS WHERE NO PHASE CHANGE TAKES PLACE

$$\frac{dV}{V} = -\int_{P_0}^{P} K_T(P)\,dP + \int_{T_0}^{T} \beta\,dT$$

Complete Equation of State



Stimulated Raman Scattering and Explosive Vaporization Induced by Laser Radiation on a Water Droplet Containing Nitrate

David H. Leach and Richard K. Chang

Yale University
New Haven, Connecticut 06520

Abstract

When micrometer-size droplets are irradiated by a visible laser beam, they can be envisioned as a lens to concentrate the incident radiation inside the droplet and as an optical cavity to provide feedback for the internally generated nonlinear radiation. Because of the concentrated internal intensity and optical feedback, the threshold for stimulated Raman scattering (SRS) from water droplets containing NH_4NO_3 can be readily achieved at low input intensity (e.g., less than 1 GW/cm^2). The SRS spectra contain the following peaks: (1) first-order SRS peaks of the stretching modes of NO_3^- and O-H; (2) nth order SRS peaks of these stretching modes with the (n-1)th order SRS as the pump source; and (3) morphology-dependent resonance peaks superimposed on the SRS of the stretching mode of O-H. Chemical species identification can be made from the energy shift of the SRS peaks. The absolute size of the droplet can be deduced from the wavelength spacing of the morphology-dependent peaks. The ratio of NO_3^- and H_2O concentration within the droplet can be qualitatively estimated from the SRS intensity

ratio of the NO_3^- mode and the O-H mode, even when the NO_3^- concentration is below 0.2 M.

At input intensities higher than that necessary to achieve SRS from a single droplet, laser-induced breakdown (LIB) can occur within the droplet shadow face. The LIB is caused by the following two processes: (1) multiphoton ionization to produce the few priming electrons and (2) cascade multiplication which rapidly increases the plasma density in subnanoseconds. Once LIB has been achieved during the rising portion of the input pulse, the transparent droplet is transformed into an optically opaque droplet which can absorb the remaining portion of the laser pulse.

LIB has been investigated in droplets containing 5 M NH_4NO_3 with a spatially resolved spectroscopic technique, which can detect the discrete emission peaks from atomic H (Balmer lines) and once ionized N and O at various locations within the plasma plumes ejected from the shadow face and the illuminated face of the droplet. Since the linear Stark parameters of H are well known, the electron density within these plumes can be estimated from the spatially varying lineshape of the H Balmer emission peak. Although the connection between LIB and electrode ignition of liquid propellents is not clear at this moment, the spectroscopic techniques we have developed to investigate the LIB associated plasma plumes from droplets should be applicable to the study of plasma ignition of liquid propellents with electrodes.

Partial support of U.S. Army Research Office (Contract No. DAAL03-87-K-0076) is acknowledged.

Stimulated Raman Scattering

and

Explosive Vaporization
Induced by Laser Radiation

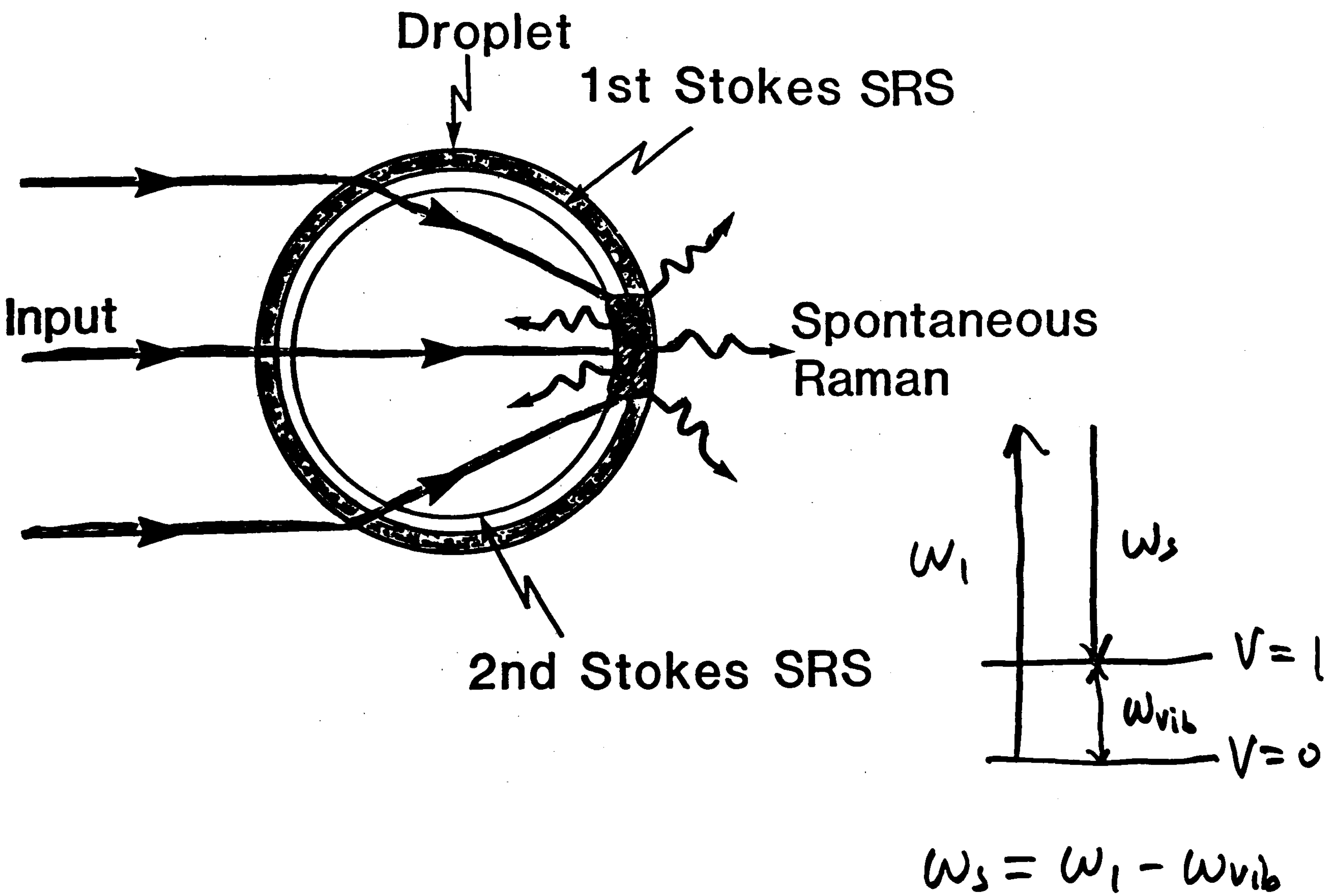
on

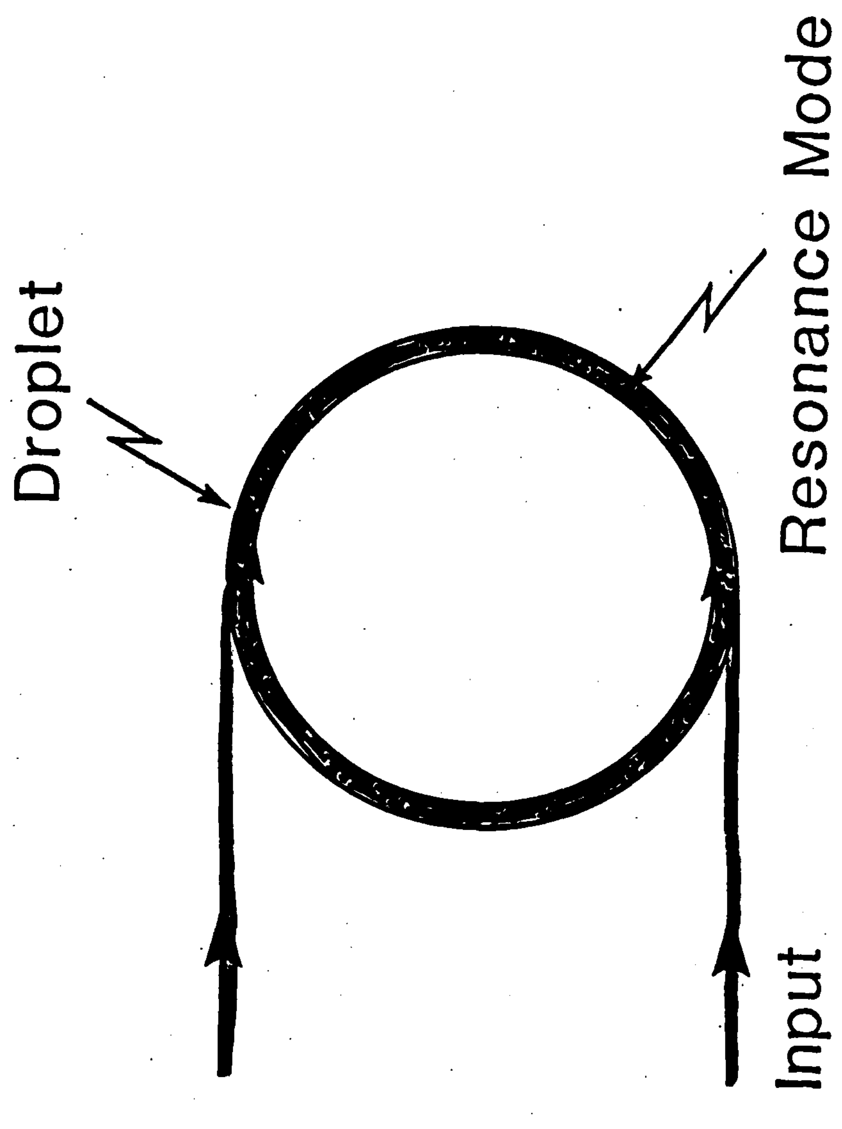
a Water Droplet Containing Nitrate

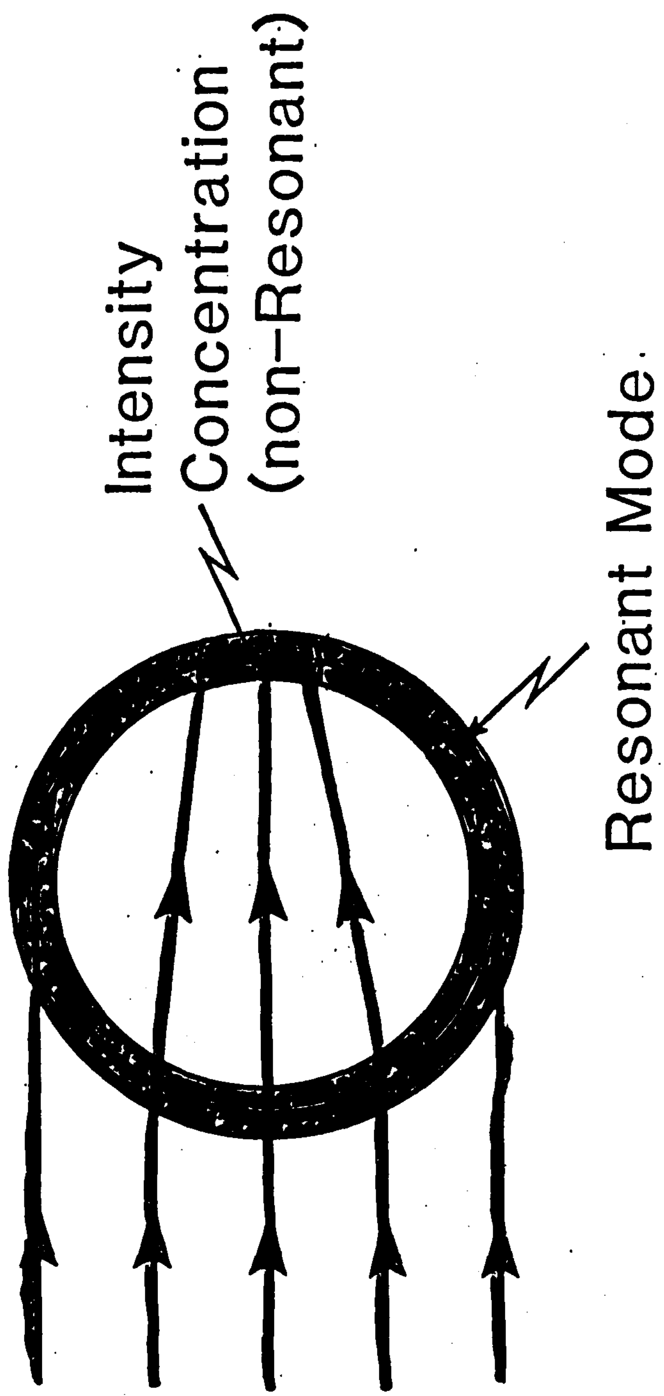
BRL
August 25, 1987

David H. Leach
Richard K. Chang

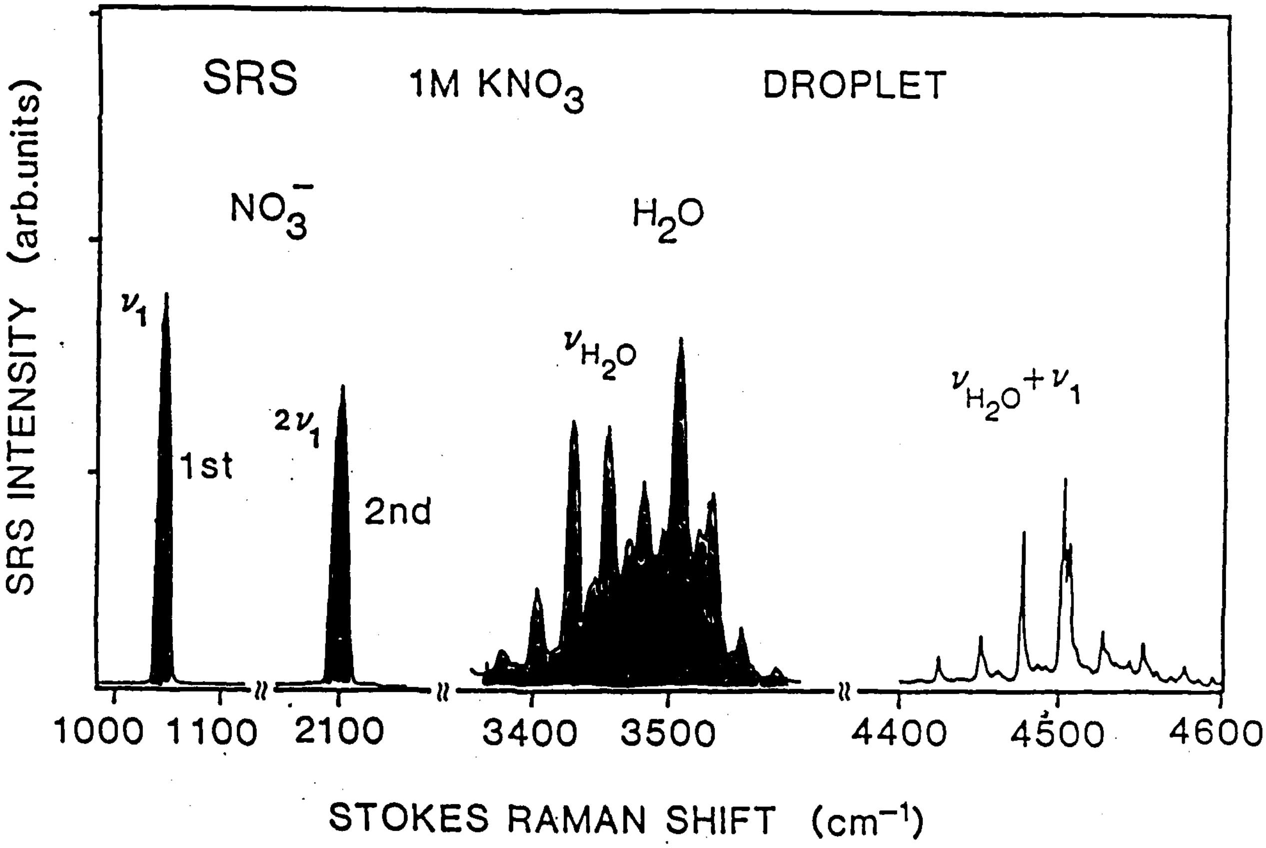
Yale University


Droplet
1st Stokes SRS
Input
Spontaneous
Raman
2nd Stokes SRS
ω_1
ω_s
$V=1$
ω_{vib}
$V=0$
$\omega_s = \omega_1 - \omega_{vib}$

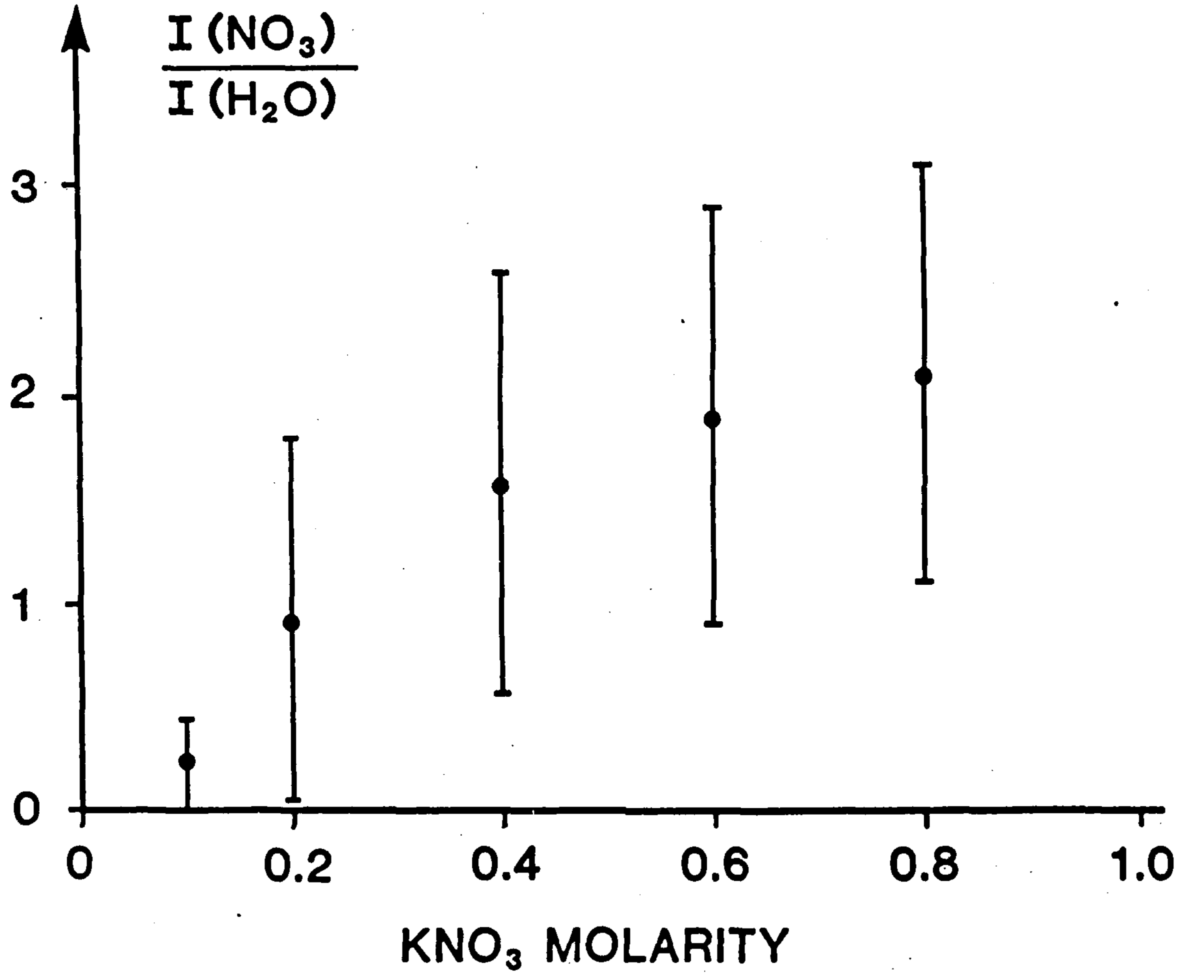

Droplet
Resonance Mode
Input



Intensity
Concentration
(non-Resonant)
Resonant Mode



SRS
1M KNO_3
DROPLET
NO_3^-
H_2O
ν_1
1st
$2\nu_1$
2nd
ν_{H_2O}
$\nu_{H_2O}+\nu_1$
SRS INTENSITY (arb.units)
1000
1100
2100
3400
3500
4400
4500
4600
STOKES RAMAN SHIFT (cm^{-1})

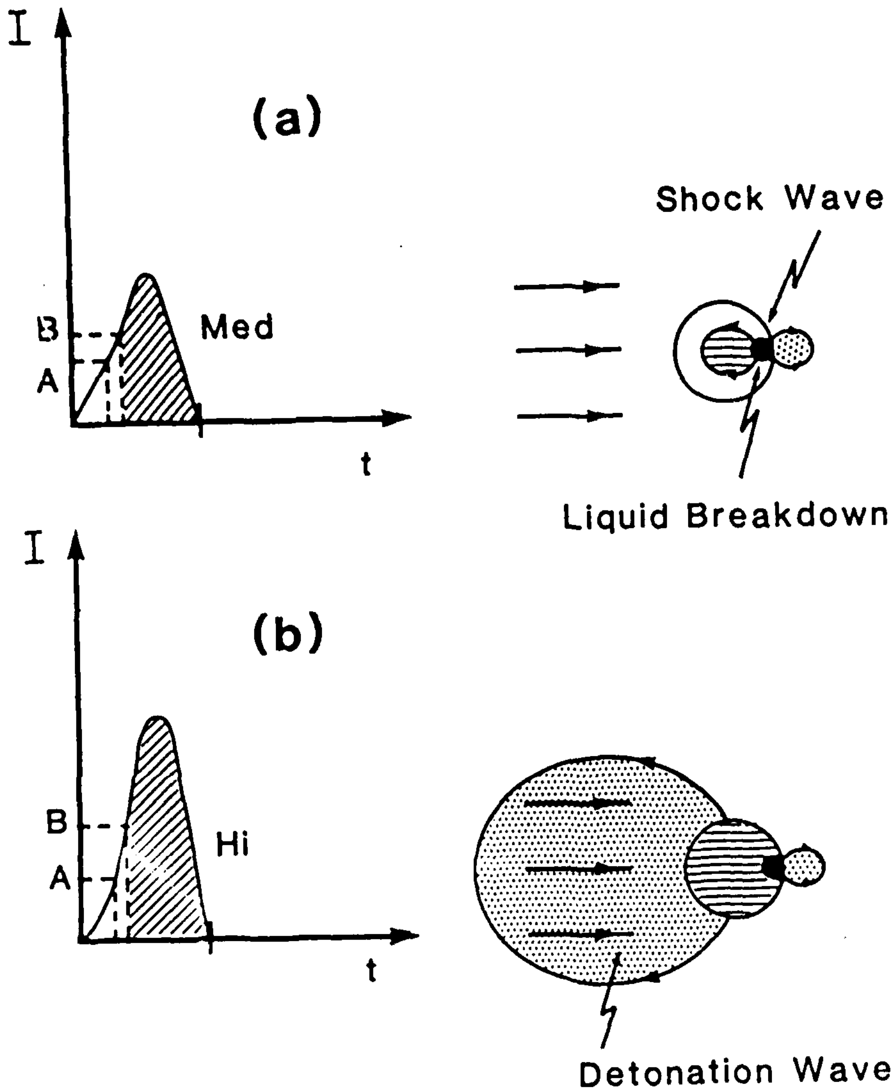


Intensity ratio of the NO_3^- mode at 1050 cm^{-1} and the O-H stretching mode at 3460 cm^{-1} as a function of the KNO_3 molarity. Each point represents the mean value of at least 10 measurements with 90% of all measurements falling within the error margin.

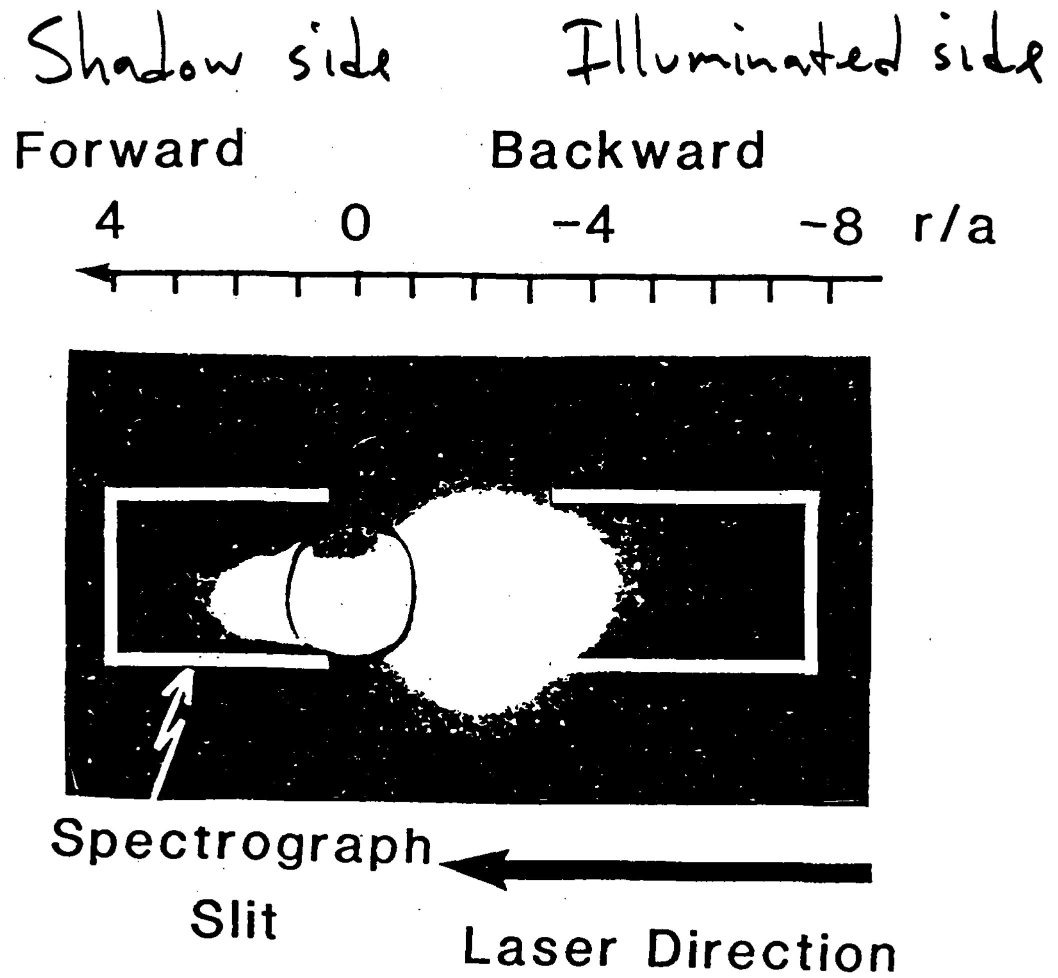
Stimulated Raman Scattering Conclusions

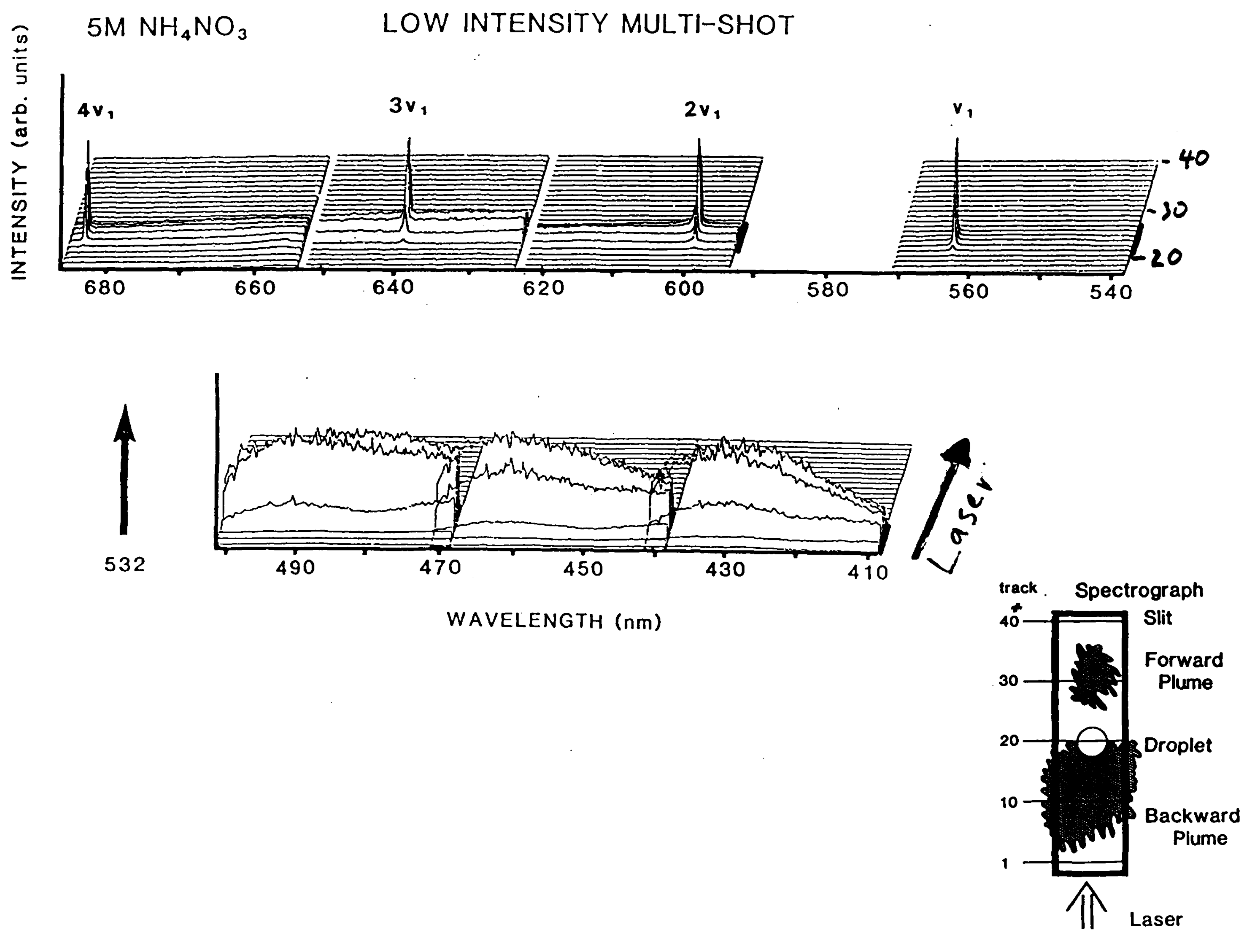
1) Species identification via molecular vibrational frequency

2) Resonance mode spacing provides size information

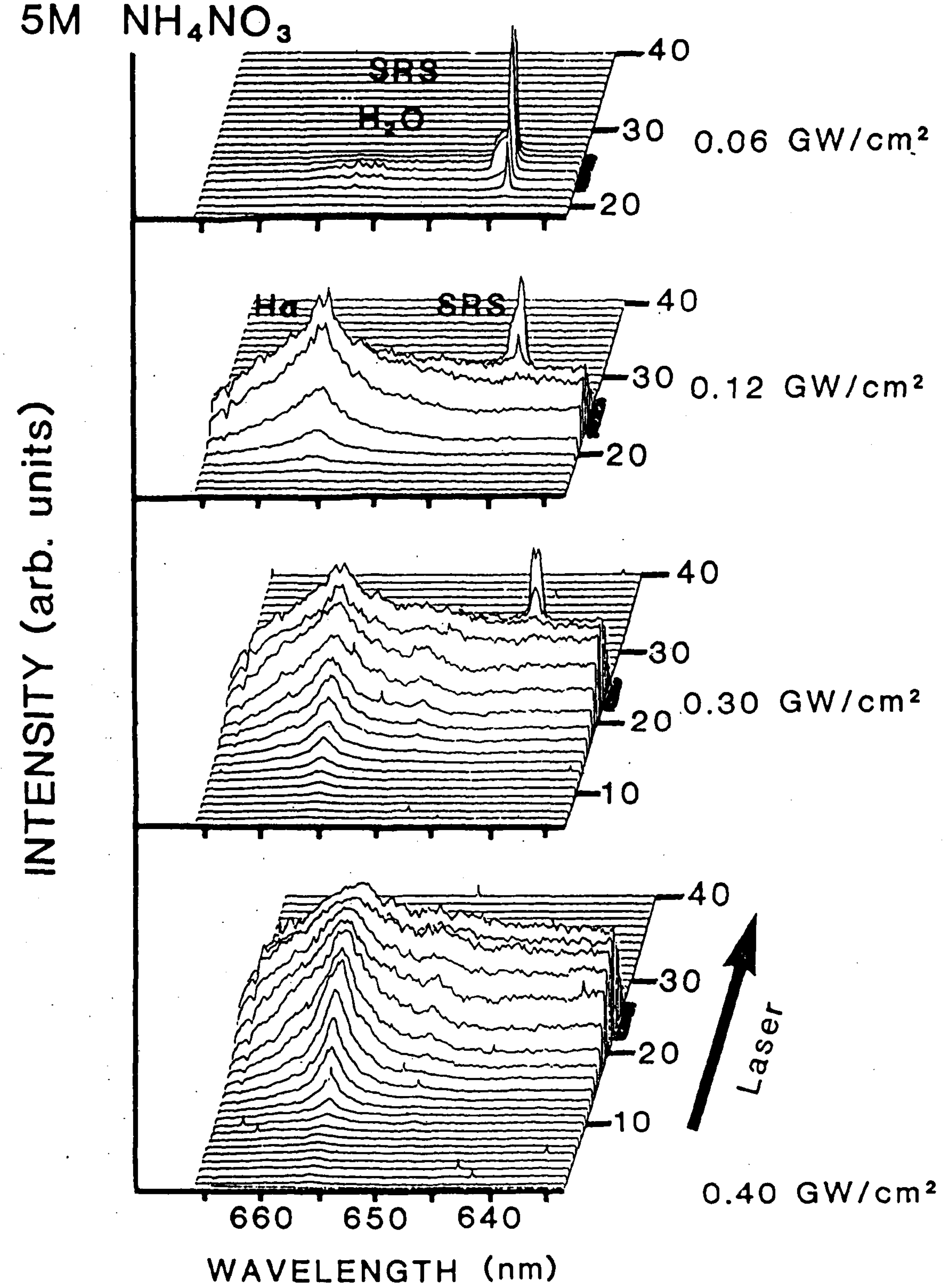


I
(a)
B
A
Med
t
Shock Wave
Liquid Breakdown
I
(b)
B
A
Hi
t
Detonation Wave

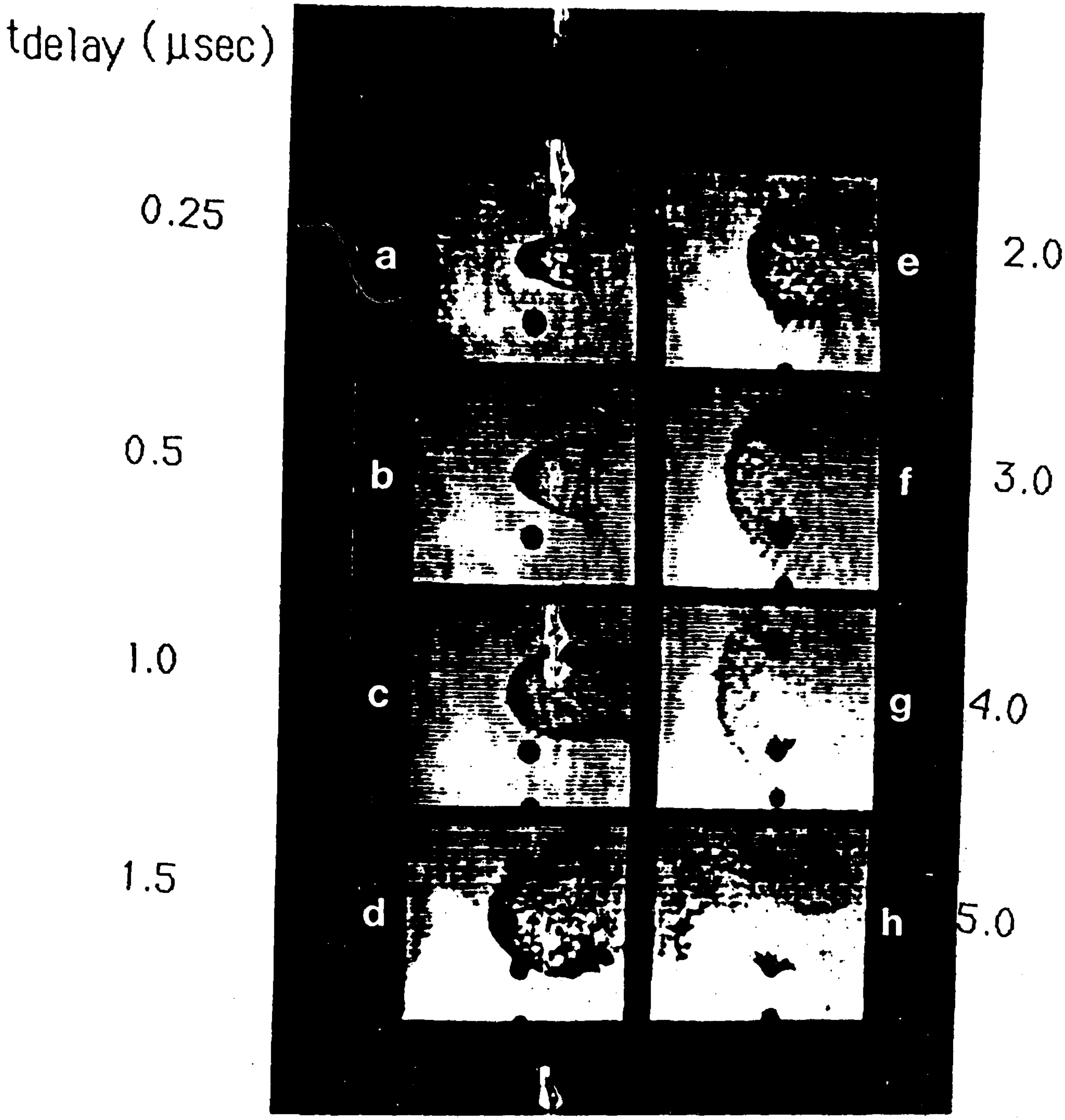

Shadow side
Illuminated side
Forward
Backward
4
0
-4
-8
r/a
Spectrograph
Slit
Laser Direction



5M NH₄NO₃
LOW INTENSITY MULTI-SHOT
INTENSITY (arb. units)
4v₁
3v₁
2v₁
v₁
40
30
20
680
660
640
620
600
580
560
540
532
490
470
450
430
410
Laser
WAVELENGTH (nm)
track
Spectrograph
Slit
Forward
Plume
Droplet
Backward
Plume
40
30
20
10
1
Laser



5M NH_4NO_3
SRS
H_2O
0.06 GW/cm²
Hα
SRS
0.12 GW/cm²
0.30 GW/cm²
0.40 GW/cm²
40
30
20
10
Laser
INTENSITY (arb. units)
660
650
640
WAVELENGTH (nm)



I_0 = 1 GW/cm2

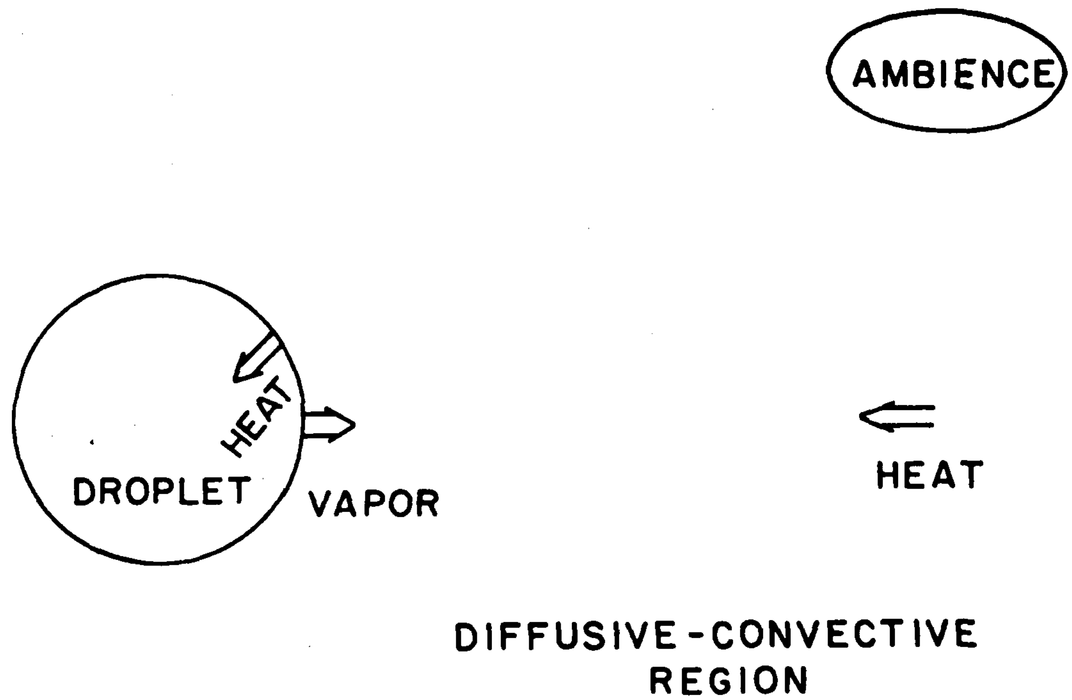
DROPLET COMBUSTION OF HAN-BASED LIQUID PROPELLANTS

C. K. LAW

UNIVERSITY OF CALIFORNIA AT DAVIS

WORK SUPPORTED BY

ARMY RESEARCH OFFICE


AMBIENCE
HEAT
DROPLET
HEAT
VAPOR
DIFFUSIVE-CONVECTIVE
REGION

OBJECTIVES

1. TO DETERMINE DROPLET EXPLOSION TEMP.

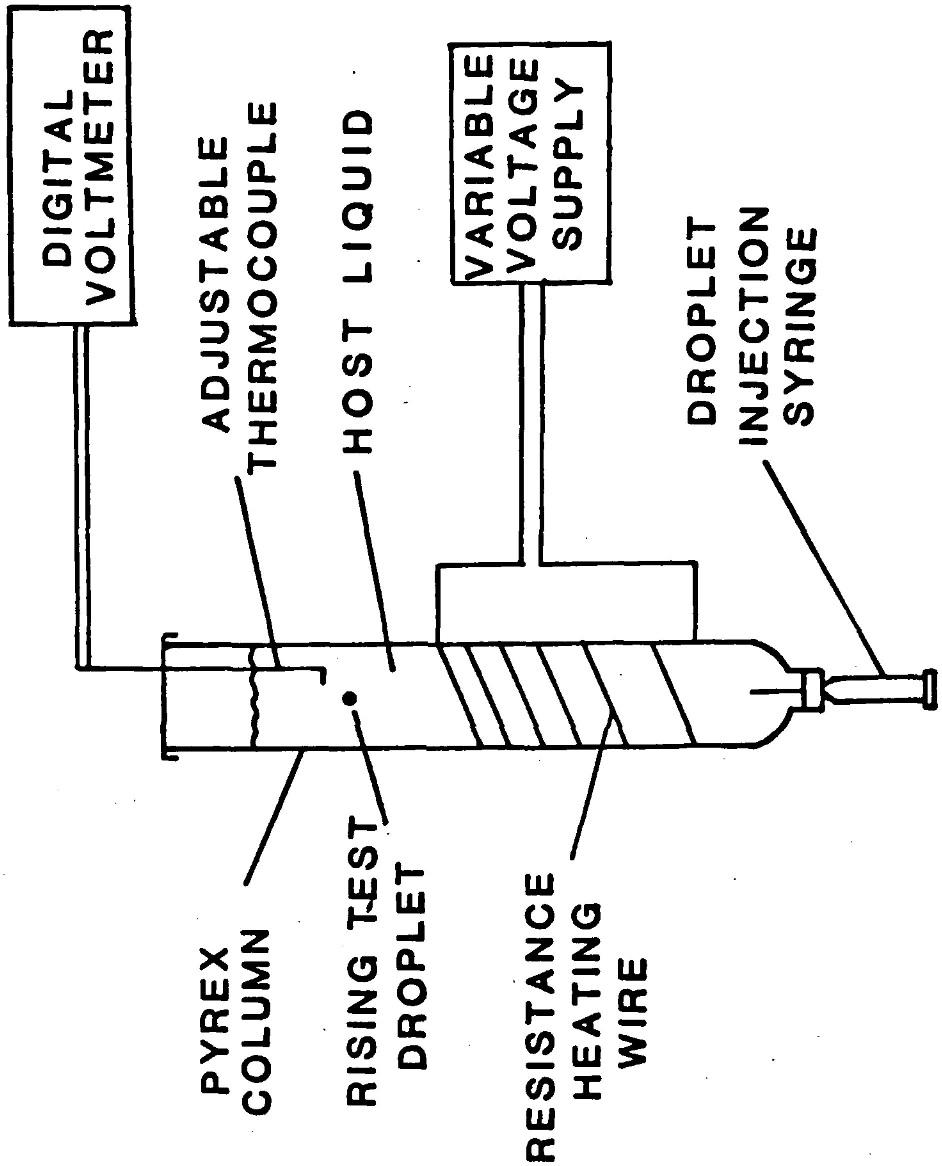
2. TO STUDY DROPLET COMBUSTION CHARACTERISTICS

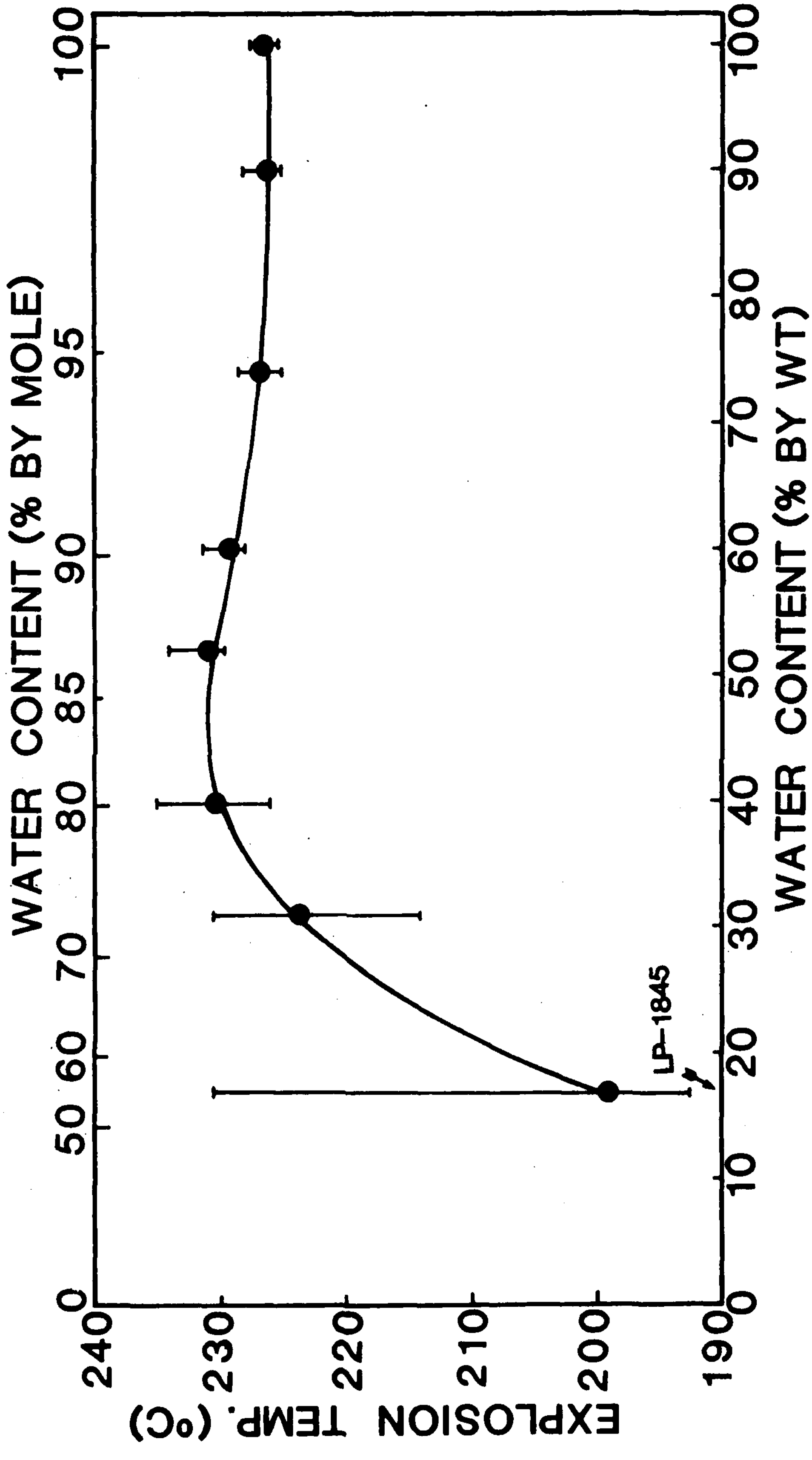
INCLUDING:

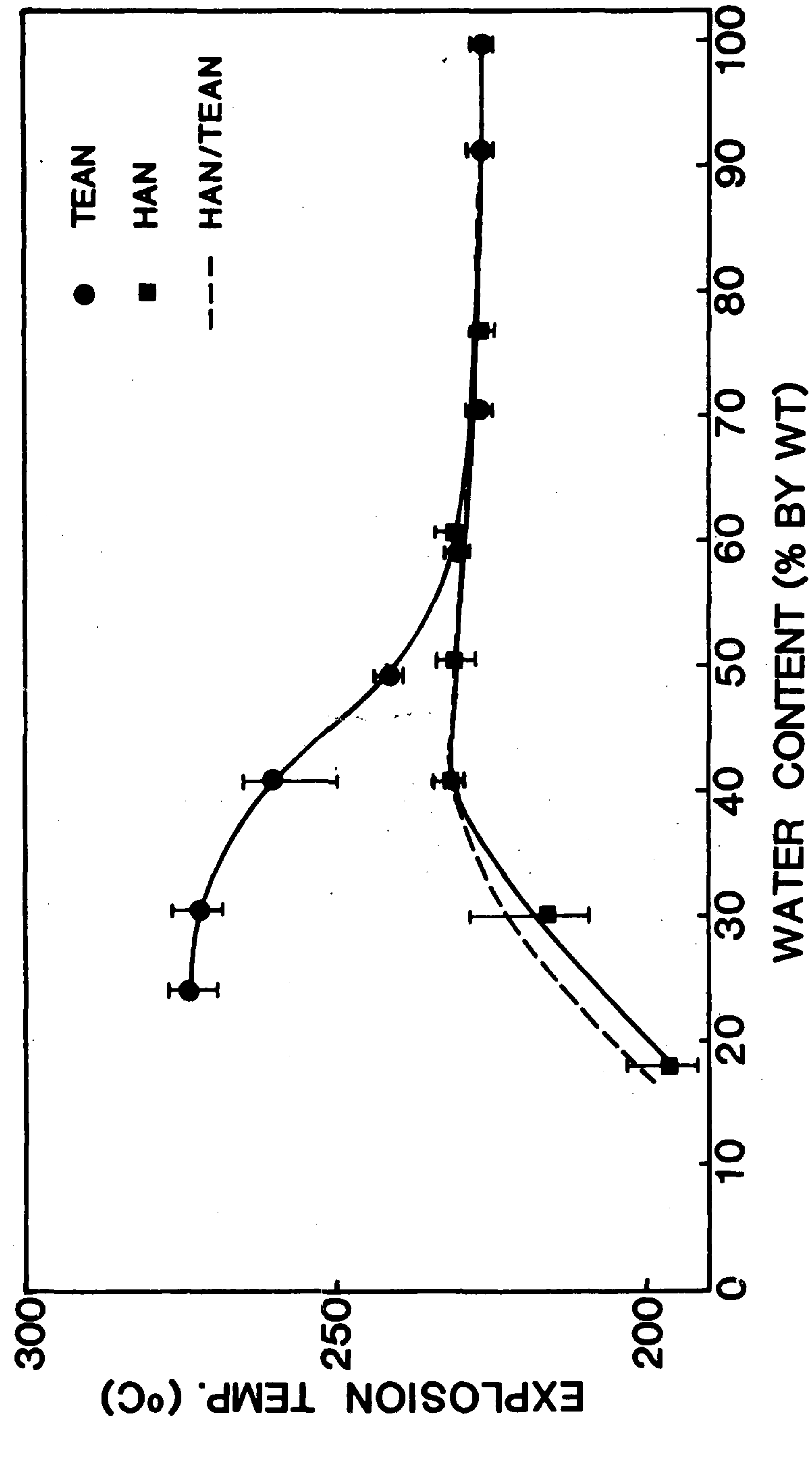
* HEAT-UP TIME
* GASIFICATION RATE
* EXPLOSION TIME/SIZE

AS FUNCTIONS OF

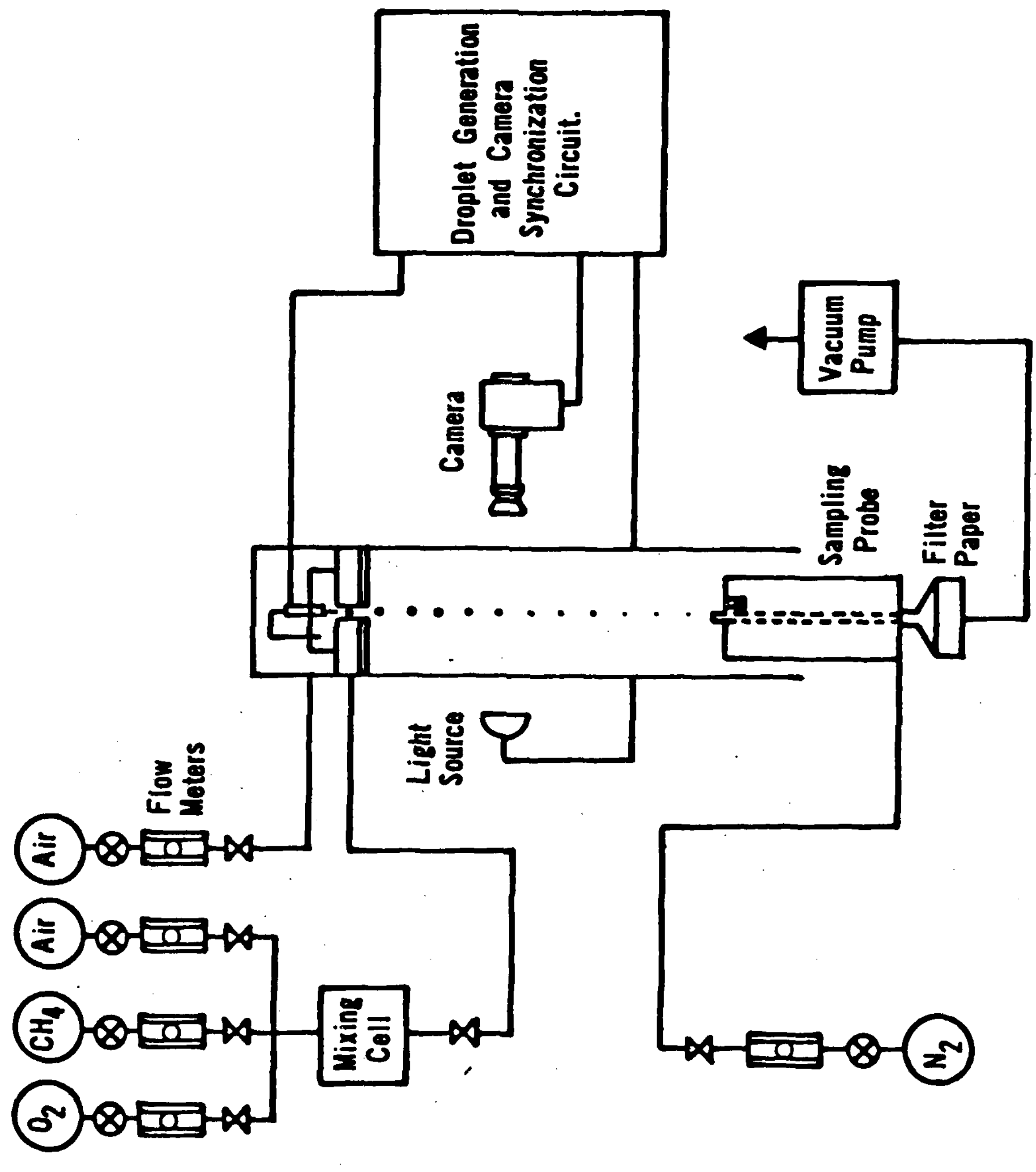
* OXYGEN CONTENT IN ENVIRONMENT
* WATER CONTENT IN PROPELLANT
* DROPLET SIZE

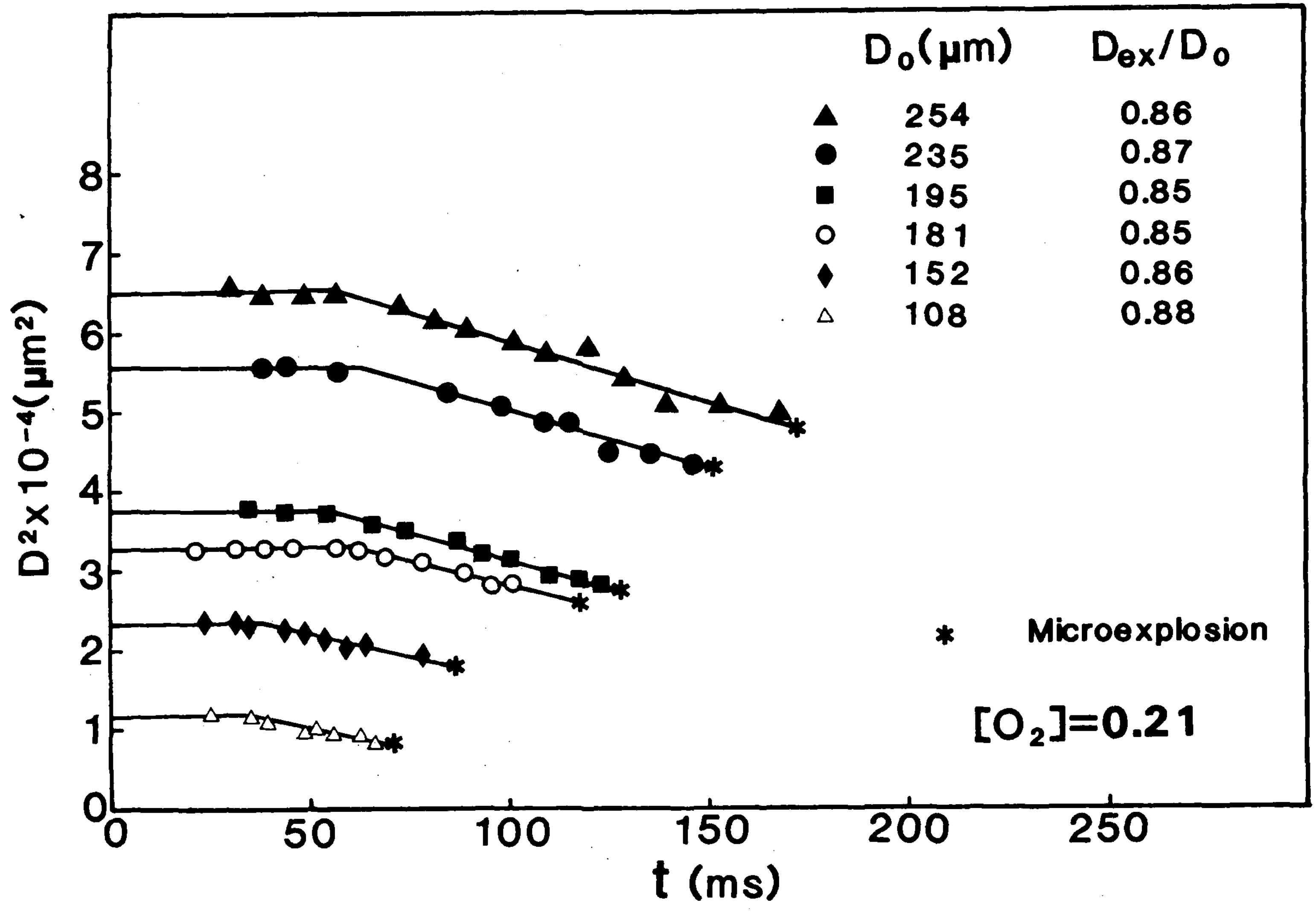

DIGITAL VOLTMETER
ADJUSTABLE THERMOCOUPLE
HOST LIQUID
VARIABLE VOLTAGE SUPPLY
DROPLET INJECTION SYRINGE
PYREX COLUMN
RISING TEST DROPLET
RESISTANCE HEATING WIRE


WATER CONTENT (% BY MOLE)
WATER CONTENT (% BY WT)
EXPLOSION TEMP. (°C)
LP-1845
0
50
60
70
80
85
90
95
100
10
20
30
40
50
60
70
80
90
100
240
230
220
210
200
190

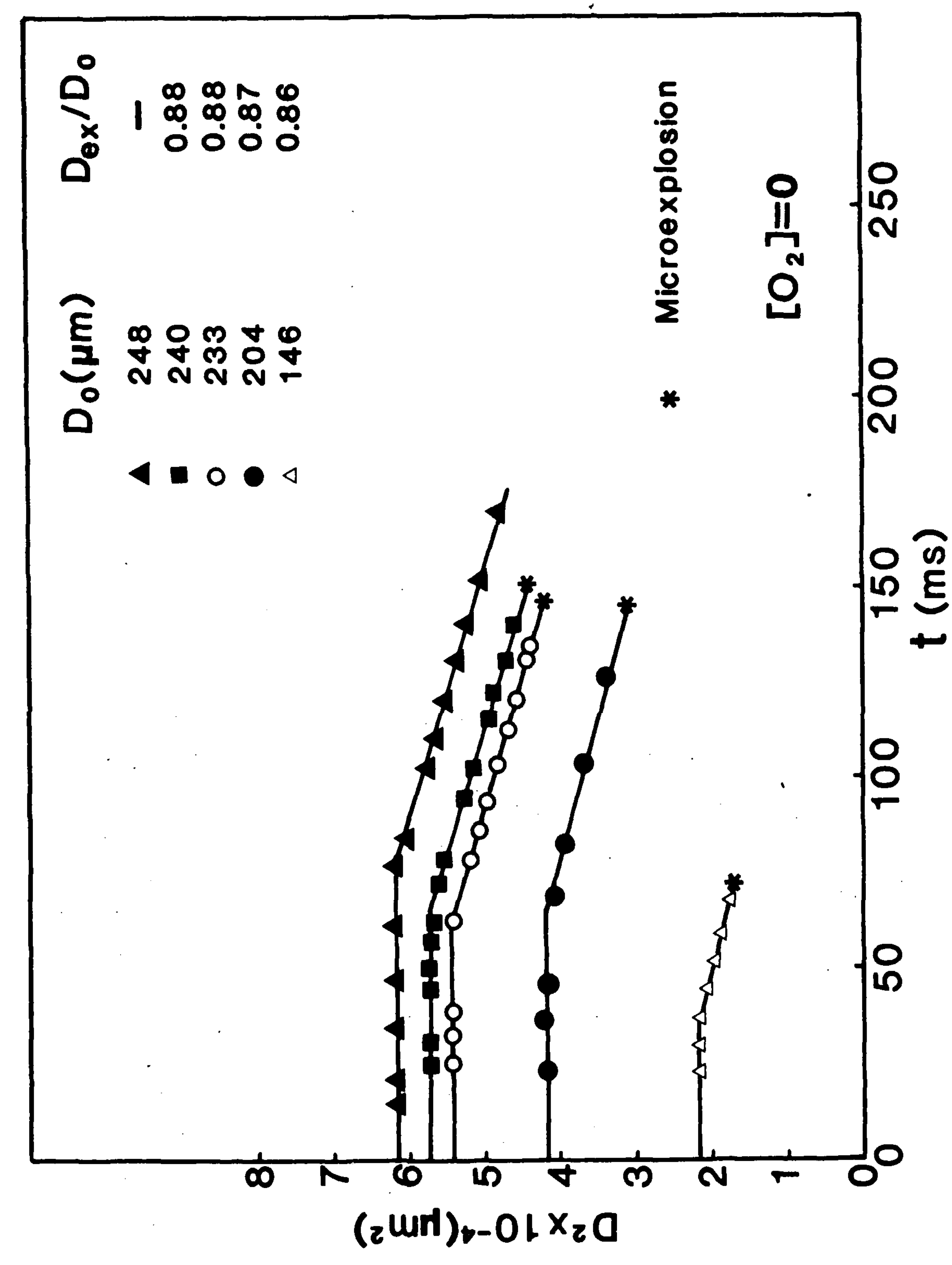


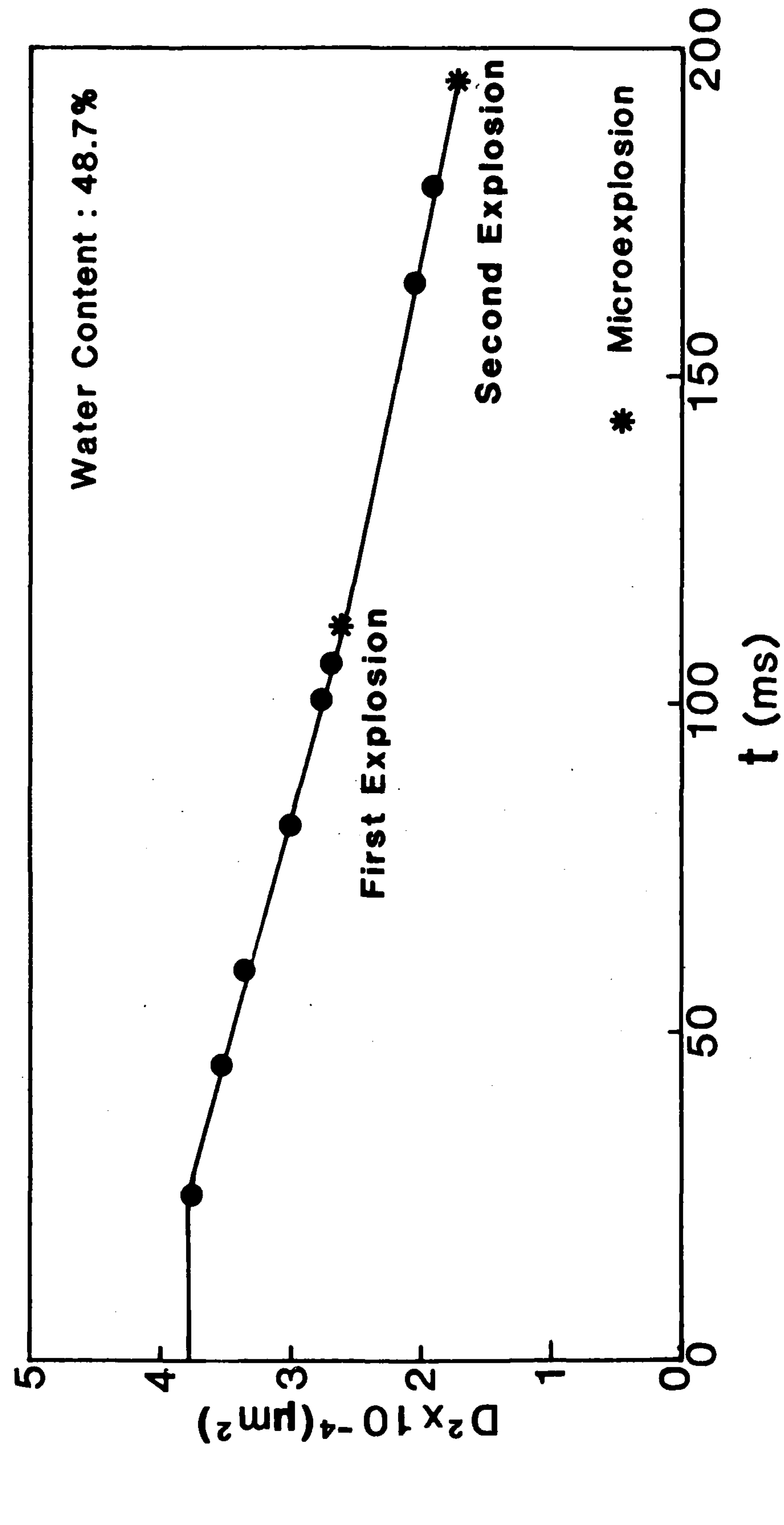
TEAN
HAN
HAN/TEAN
WATER CONTENT (% BY WT)
EXPLOSION TEMP. (°C)
0
10
20
30
40
50
60
70
80
90
100
200
250
300


Droplet Generation and Camera Synchronization Circuit.
Camera
Vacuum Pump
Sampling Probe
Filter Paper
Light Source
Flow Meters
Air
Air
CH_4
O_2
Mixing Cell
N_2

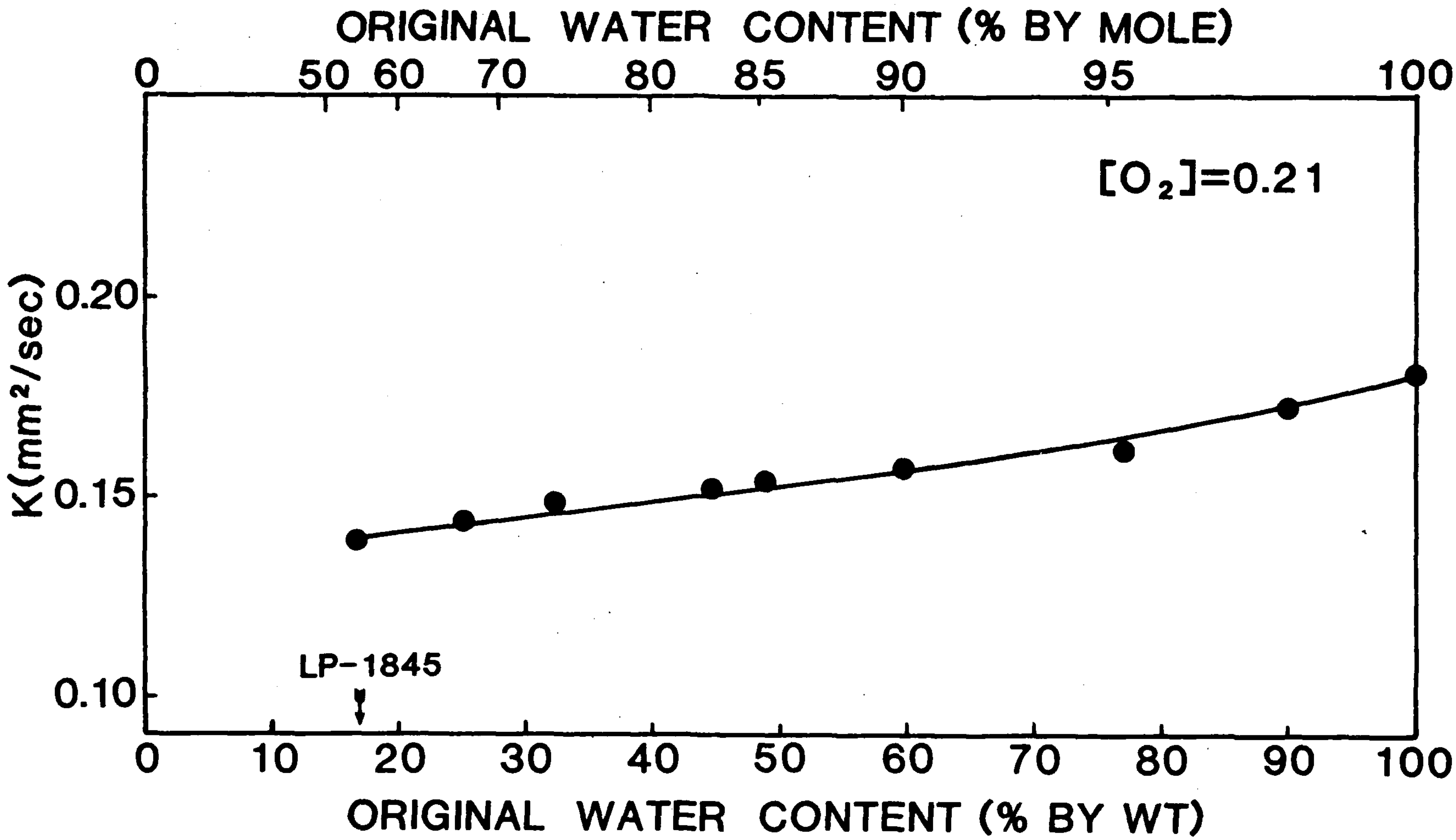


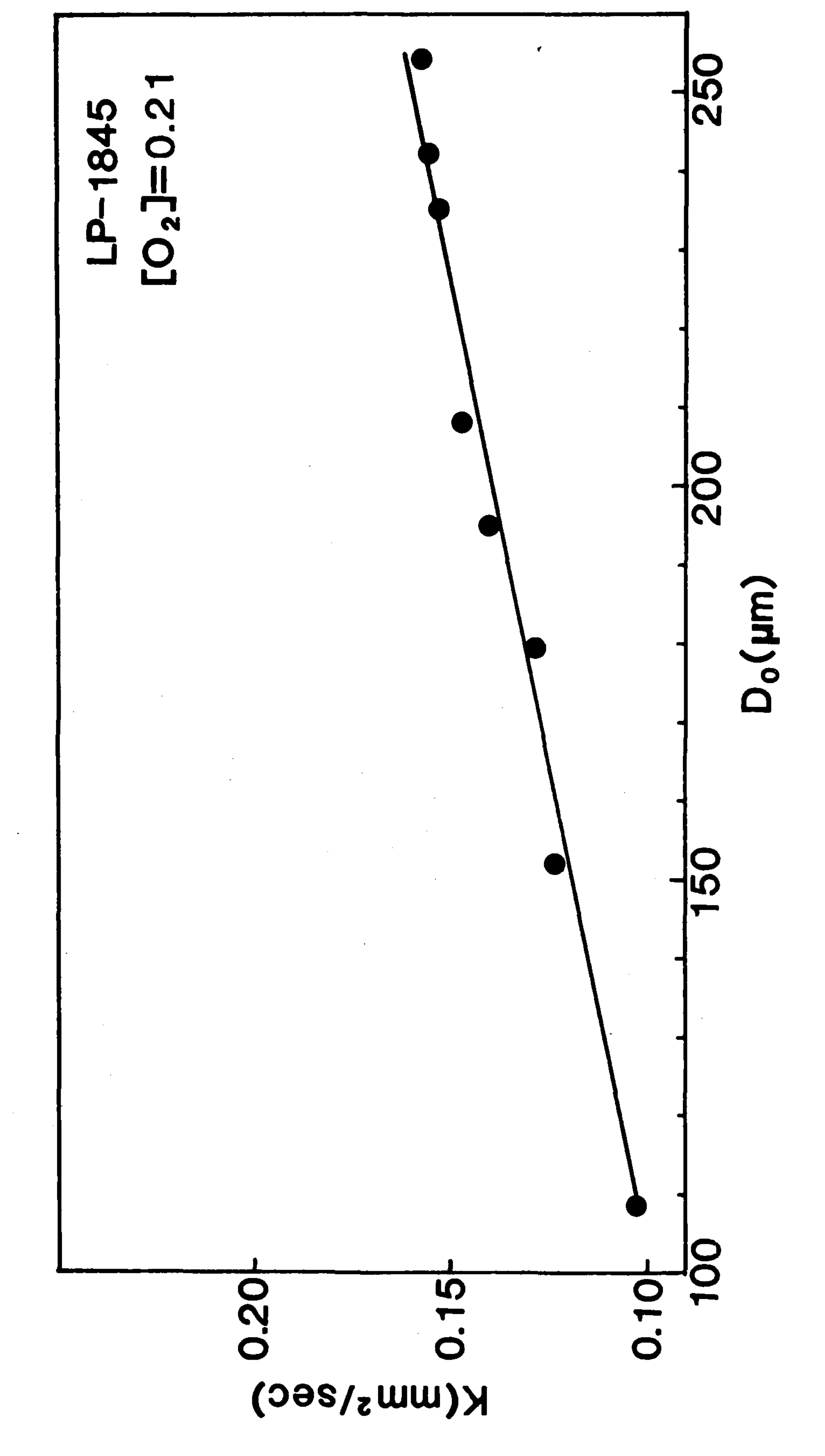
D_o(μm)
D_{ex}/D_o
254 0.86
235 0.87
195 0.85
181 0.85
152 0.86
108 0.88
* Microexplosion
$[O_2]=0.21$
$D^2 \times 10^{-4}$(μm^2)
t (ms)
0
50
100
150
200
250
1
2
3
4
5
6
7
8


D_o(μm)
248
240
233
204
146
D_{ex}/D_o
—
0.88
0.88
0.87
0.86
* Microexplosion
$[O_2]=0$
t (ms)
0
50
100
150
200
250
$D^2 \times 10^{-4}$(μm²)
0
1
2
3
4
5
6
7
8

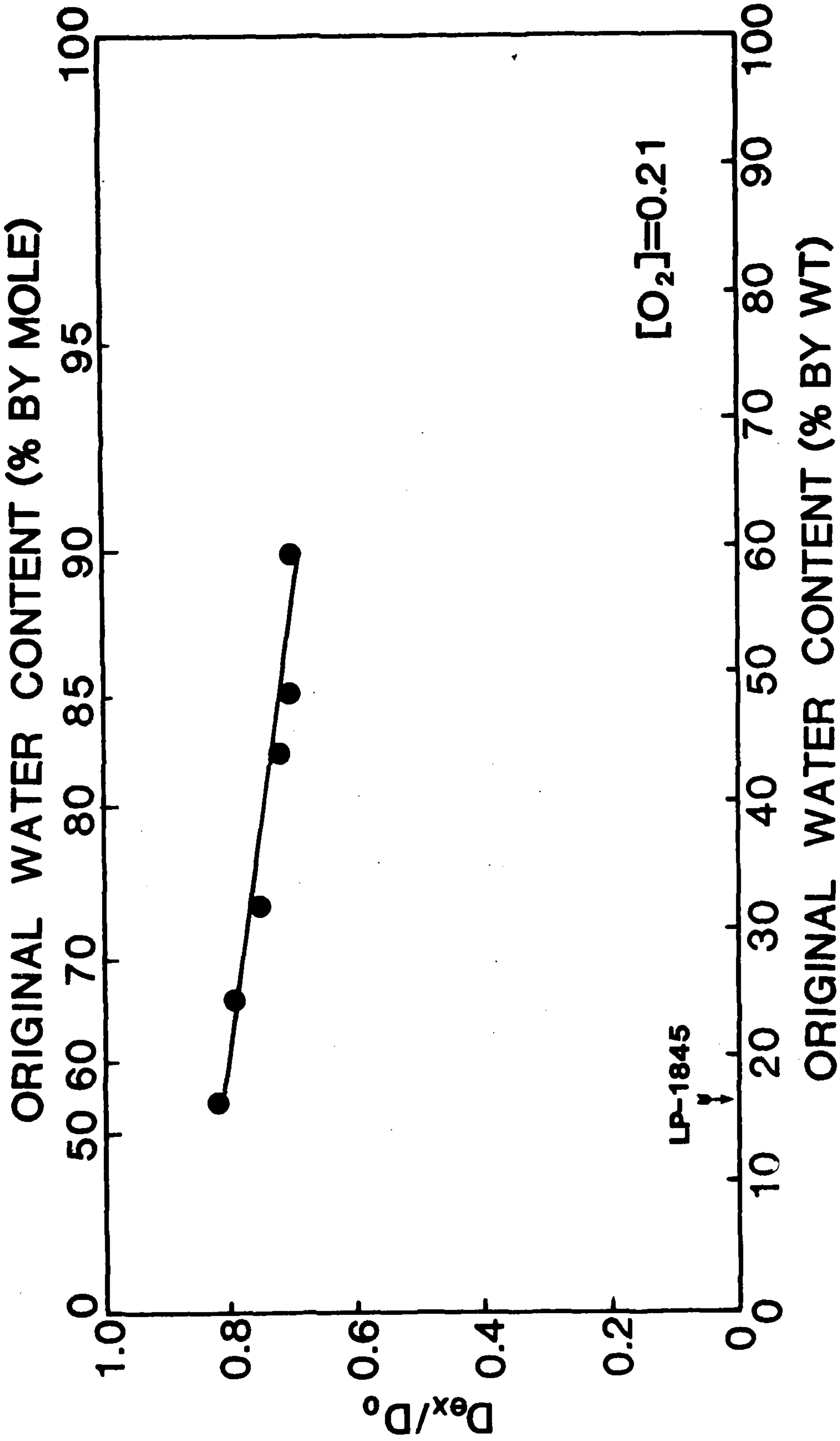


Water Content : 48.7%
First Explosion
Second Explosion
* Microexplosion
$D^2 \times 10^{-4} (\mu m^2)$
t (ms)
0
1
2
3
4
5
0
50
100
150
200


ORIGINAL WATER CONTENT (% BY MOLE)
0
50
60
70
80
85
90
95
100
[O₂]=0.21
K(mm²/sec)
0.20
0.15
0.10
LP-1845
0
10
20
30
40
50
60
70
80
90
100
ORIGINAL WATER CONTENT (% BY WT)

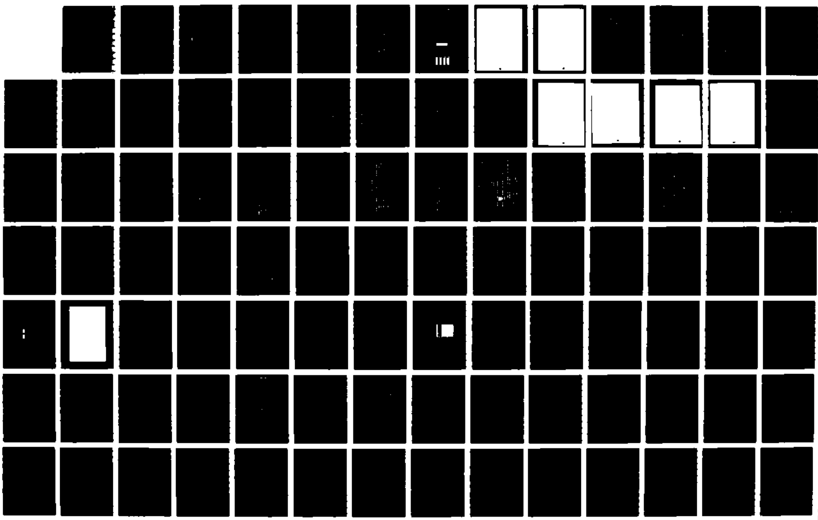


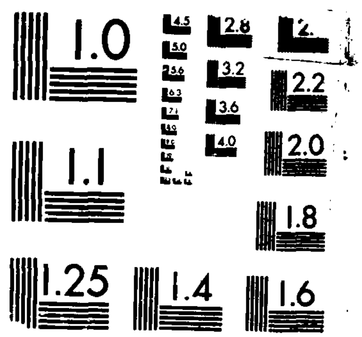
LP-1845
[O₂]=0.21
K(mm²/sec)
0.10
0.15
0.20
100
150
200
250
D₀(μm)



ORIGINAL WATER CONTENT (% BY MOLE)
ORIGINAL WATER CONTENT (% BY WT)
D_{ex}/D_o
$[O_2]=0.21$
LP-1845
0
50
60
70
80
85
90
95
100
0
10
20
30
40
50
60
70
80
90
100
1.0
0.8
0.6
0.4
0.2
0

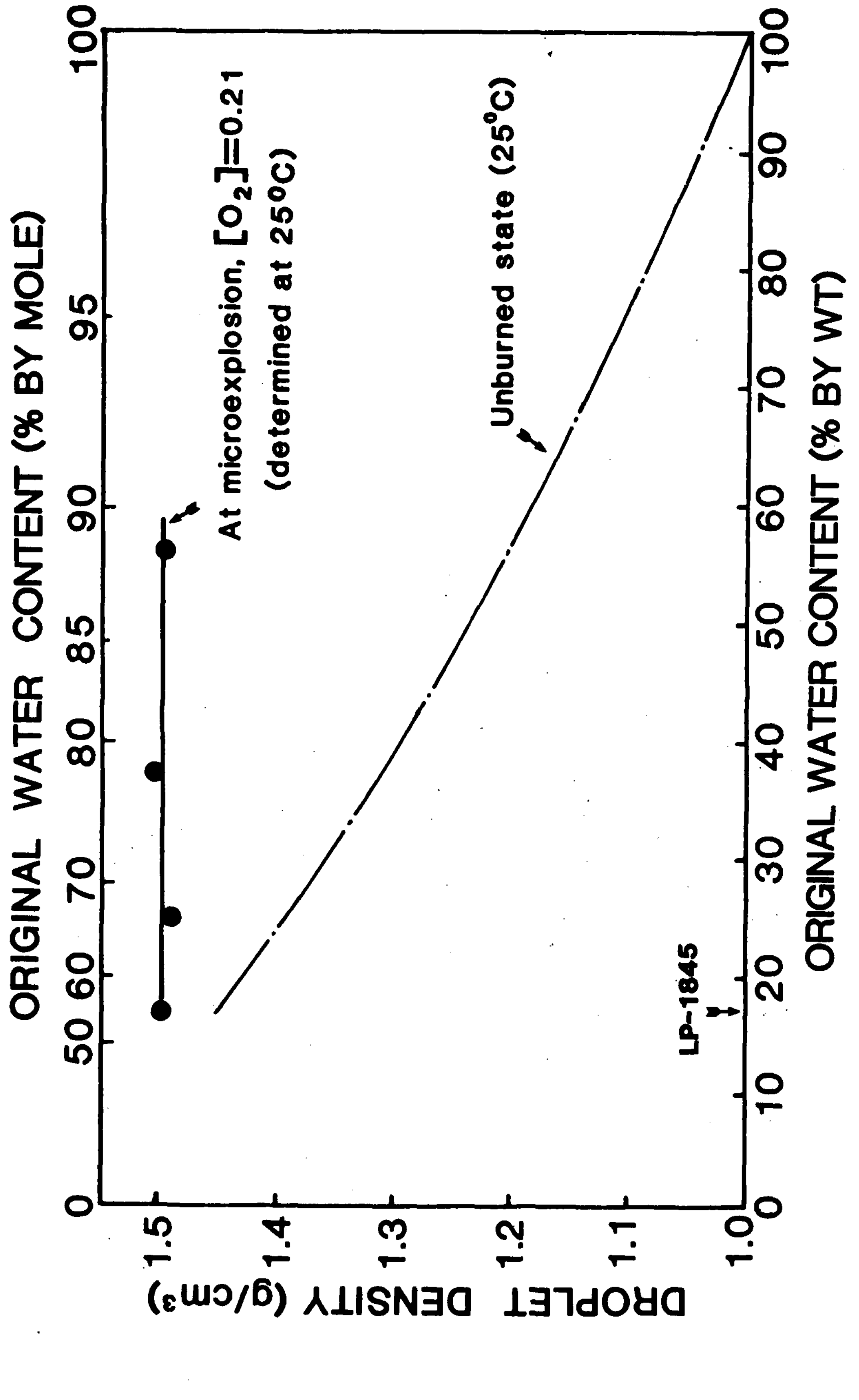
AD-A194 679 THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS 2/3
(3RD) HELD IN ABERD..(U) ARMY BALLISTIC RESEARCH LAB
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL. MAR 88
UNCLASSIFIED BRL-SP-73 F/G 19/1 NL





MICROCOPY RESOLUTION TEST CHART

UREAU STANDARDS-1963-A


ORIGINAL WATER CONTENT (% BY MOLE)
0
50
60
70
80
85
90
95
100
At microexplosion, [O2]=0.21
(determined at 25°C)
Unburned state (25°C)
LP-1845
ORIGINAL WATER CONTENT (% BY WT)
0
10
20
30
40
50
60
70
80
90
100
DROPLET DENSITY (g/cm³)
1.0
1.1
1.2
1.3
1.4
1.5

SUMMARY (1)

A. DROPLET EXPLOSION TEMP. EXPERIMENT

1. EXPLOSION TEMP. AROUND 200°C

2. EXPLOSION INDUCED BY

   * LIQUID-PHASE REACTION FOR WATER CONTENTS LESS THAN 30-40 PERCENT

   * HOMOGENEOUS NUCLEATION OF WATER FOR HIGHER WATER CONTENTS

3. HAN INITIATES LIQUID-PHASE REACTION

SUMMARY (2)

B. DROPLET COMBUSTION EXPERIMENT

1. INITIAL DROPLET HEATING PERIOD INCREASES WITH INCREASIMG SALT CONCENTRATION
2. WATER IS THE DOMINANT VAPORIZING SPECIES
3. MILD LIQUID-PHASE REACTION EXISTS
4. A CRITICAL SALT CONCENTRATION (1.5 g/cm^3) SEEMS TO EXIST AT WHICH DROPLET MICROEXPLOSION OCCURS

DSC OF LIQUID PROPELLANTS AND CRYSTALLINE HAN

Leon Decker and R.A. Fifer
U.S. Army Ballistic Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ABSTRACT

A DSC stability test has been developed for monitoring the stability of HAN-based liquid propellants, and the destabilizing effects of metal impurities. The test involves simultaneous ignition temperature (Tig) measurements for eight samples (2.3 mg each) heated in glass capillaries in a DSC pressurized to 6.9 MPa (1000 psi). Data are given for neat propellant "1845", as well as for samples of the propellant "doped" with 3-150 ppm of iron or copper. The results show that 5 or 10 ppm of either metal leads to a measurable decrease in Tig, and that the decrease in Tig per unit metal concentration is greatest at the lowest metal concentrations. From the signs and shapes of the DSC peaks under different conditions, it thus been found that when water vaporization is suppressed, there are no detectable endo- or exotherms prior to ignition, and that the first gas-producing reaction is apparently endothermic. When water vaporization is suppressed, the Tig for HAN-based propellants are much higher (>200^{o}C) than previously suspected.

A preliminary examination of two crystalline forms of HAN indicate that the heats of fusion of both forms (alpha-HAN = 27.0 +/- 1.8 cal/gm; beta-HAN = 26.7 +/- 1.8 cal/gm) are, within experimental limits, identical. Much more work needs to be performed to properly characterize the experimental material.

DSC STABILITY TEST FOR LIQUID PROPELLANTS

AN UPDATE

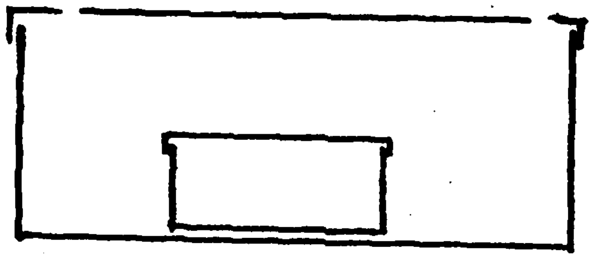
WHY: ONSET TEMPERATURE IS A QUICK GAUGE OF "QUALITY"

PROVIDES A MEANS OF DETERMINING DETERIORATION DUE TO AGING AND/OR TRANSITIONAL METAL IMPURITIES

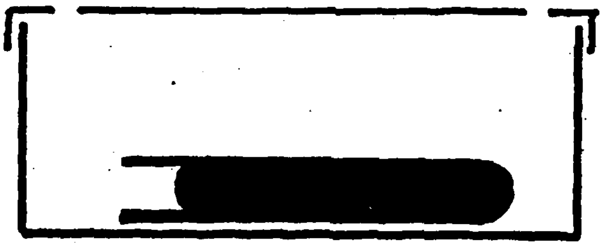
REF: R.A. FIFER, L.J. DECKER, P.J. DUFF, "DSC STABILITY TEST FOR LIQUID PROPELLANTS",22nd JANNAF COMBUSTION MEETING, CPIA PUB. 432,VOL. II, P. 203, OCTOBER, 1985

SAMPLE CONFIGURATIONS:

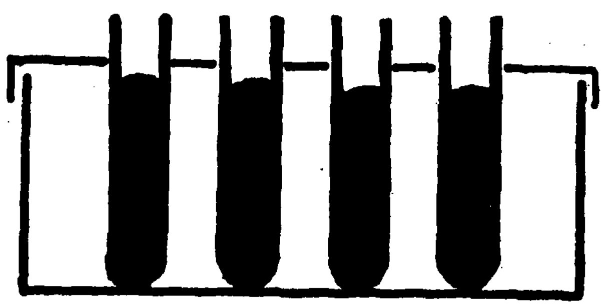
METAL PAN (GOLD, ALUMINUM, PLATINUM)

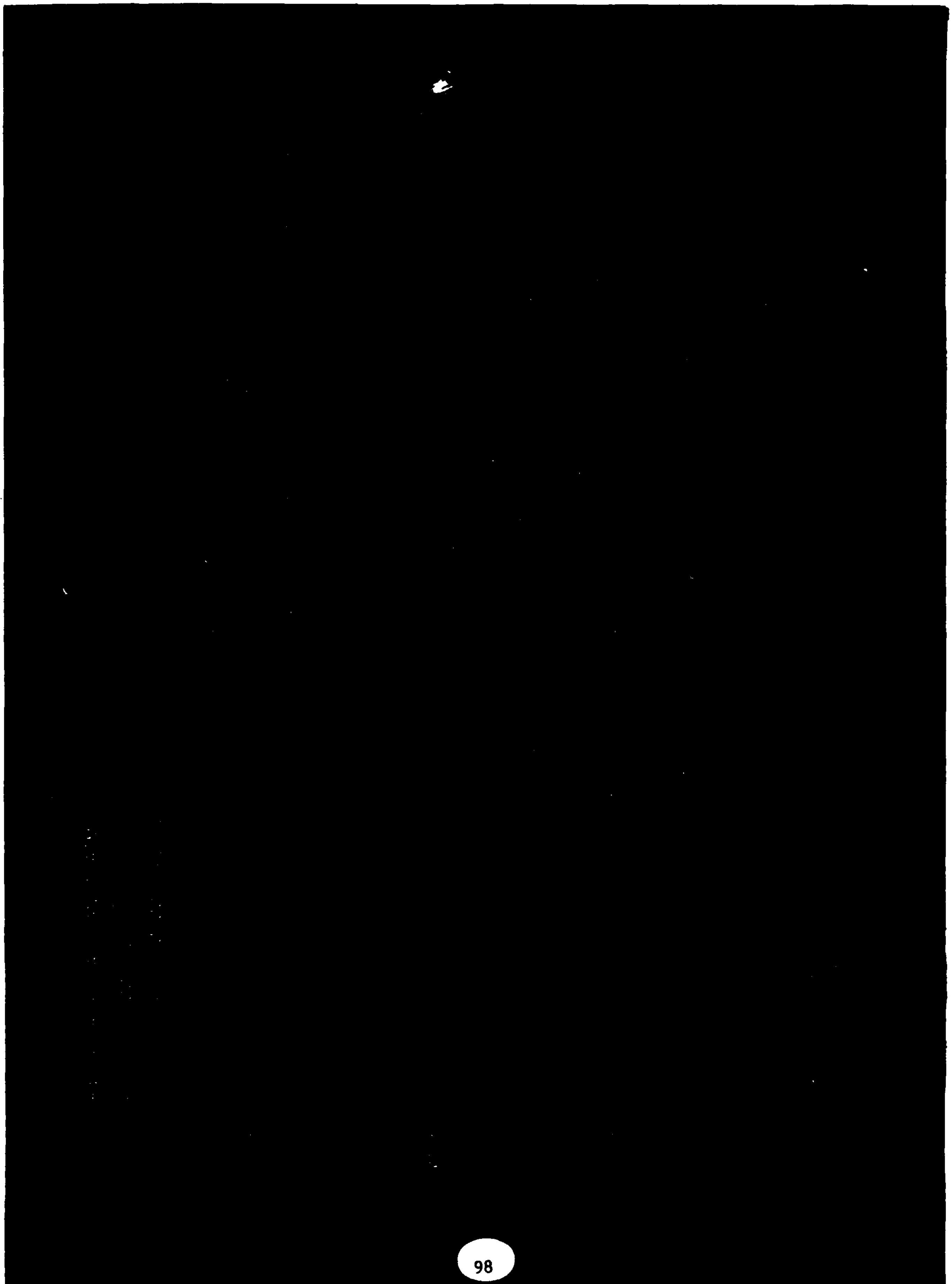


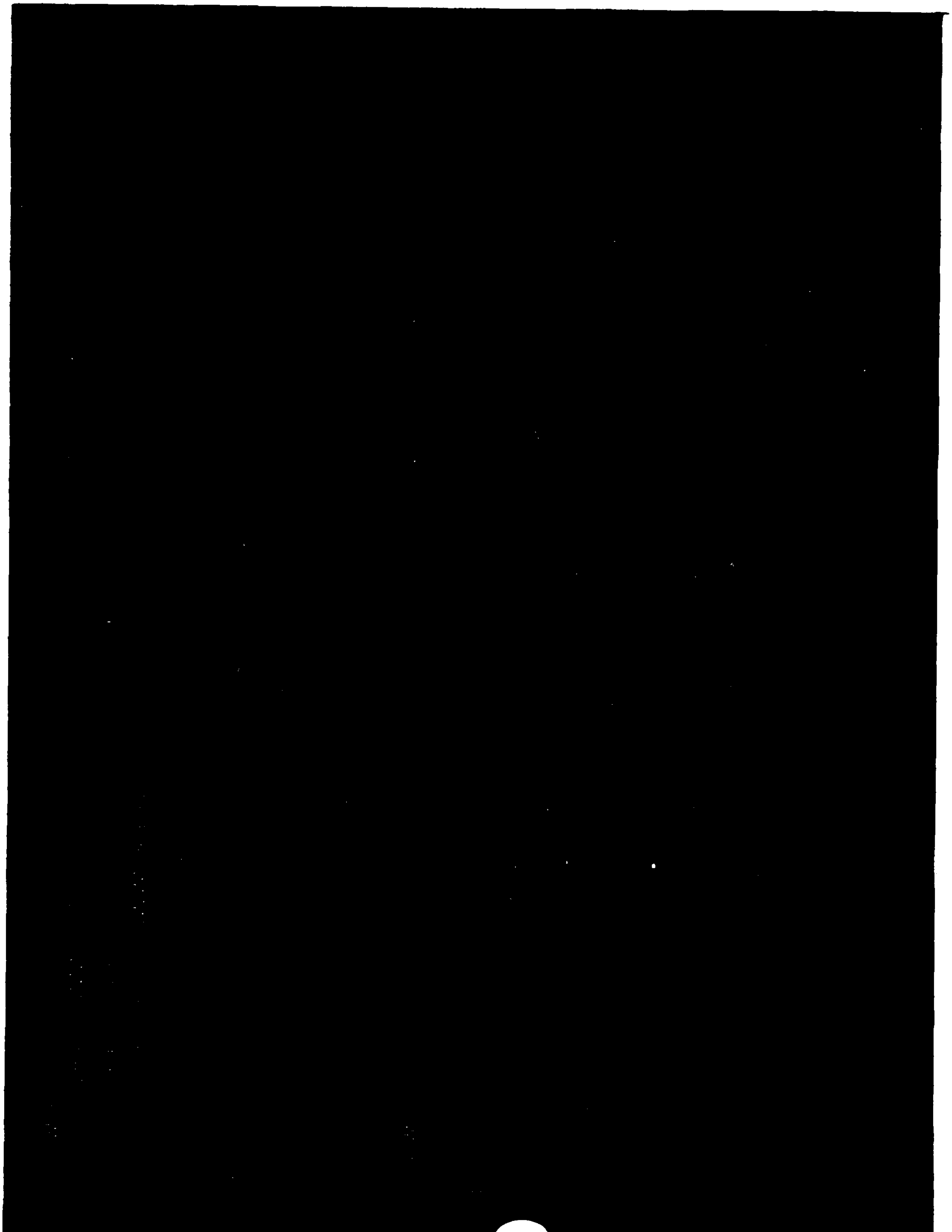
HORIZONTAL CAPILLARY: 4MM X 1.2MM I.D.



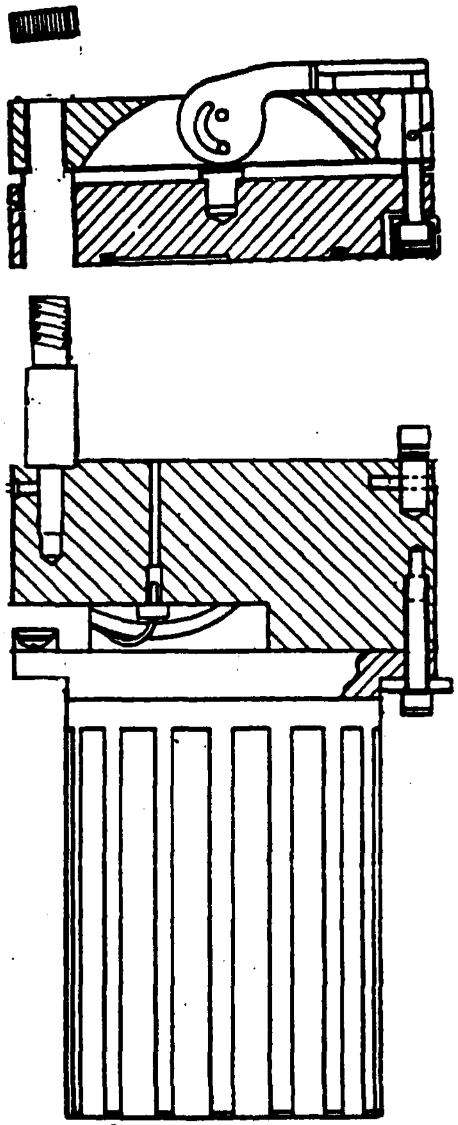
VERTICAL CAPILLARIES (MULTIPLE SAMPLES)



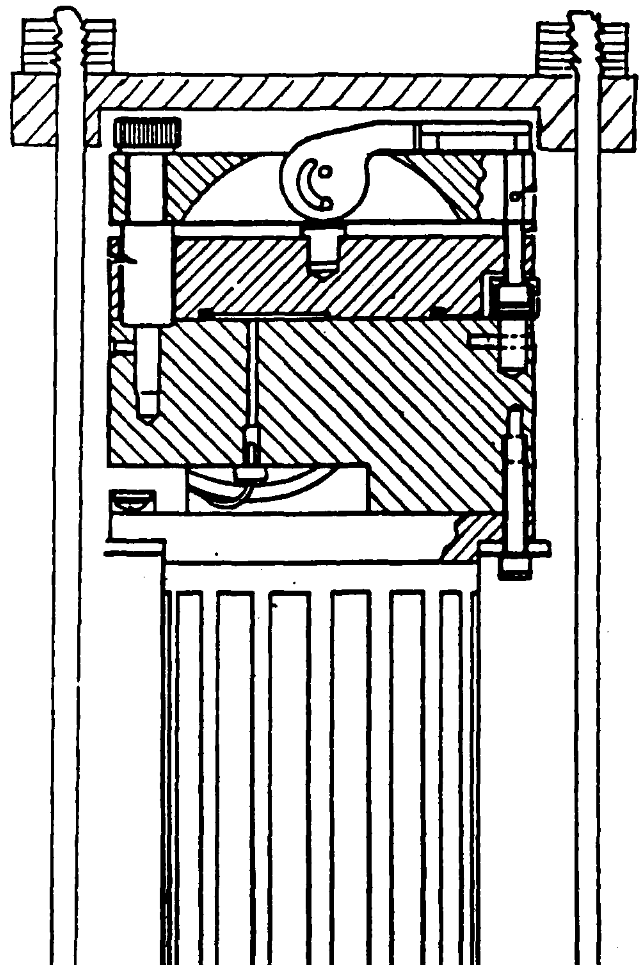


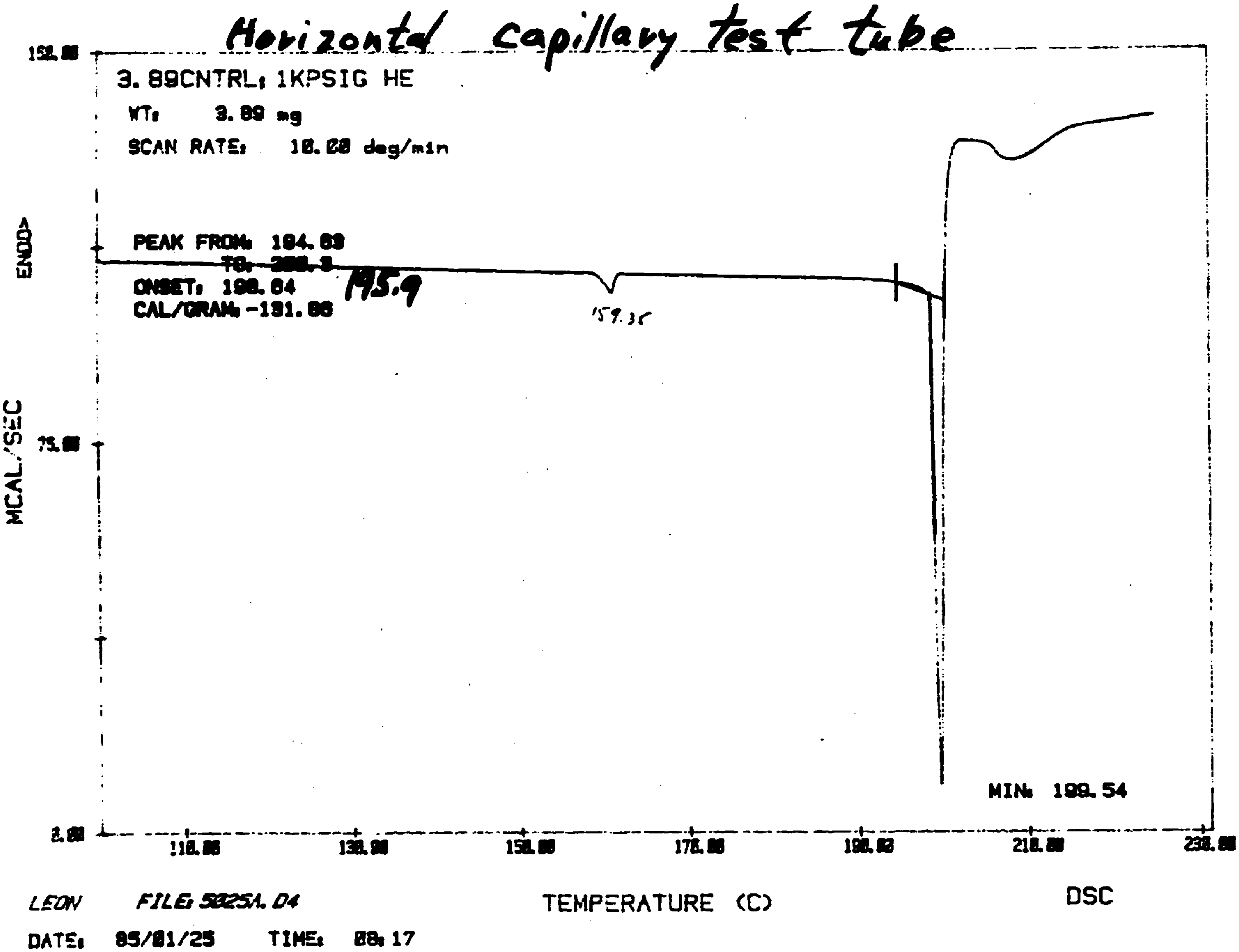


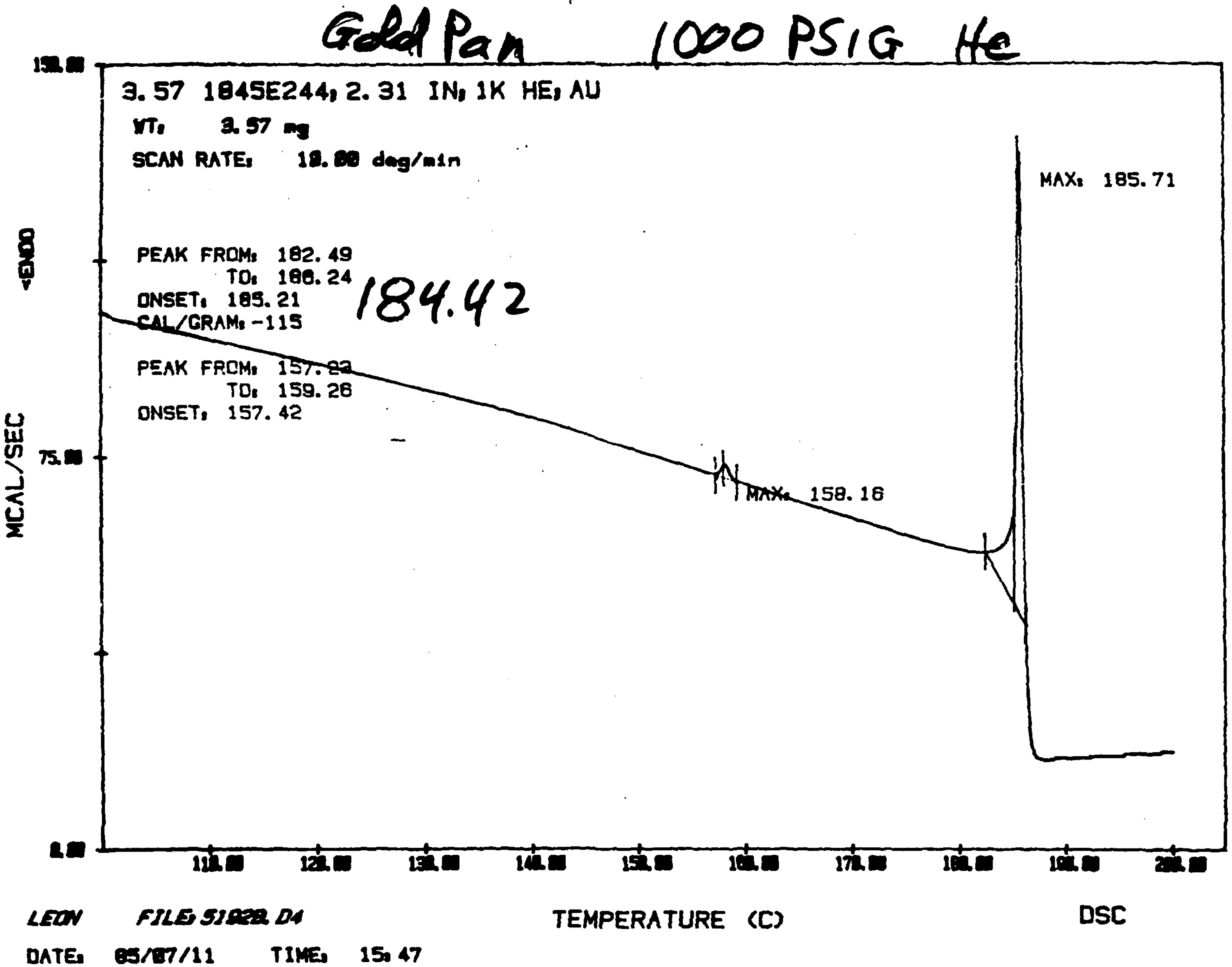
PERKIN-ELMER DSC HEAD

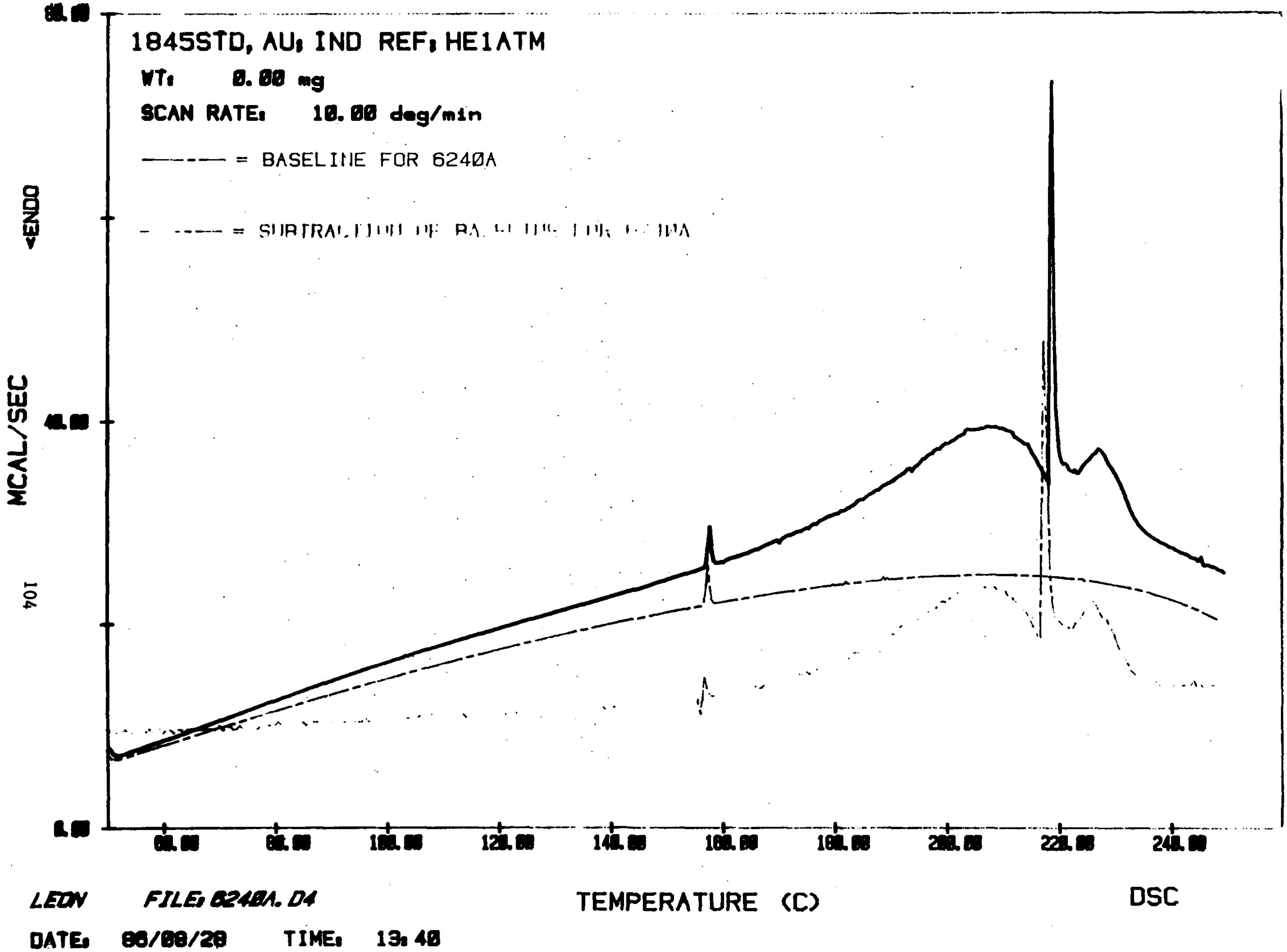


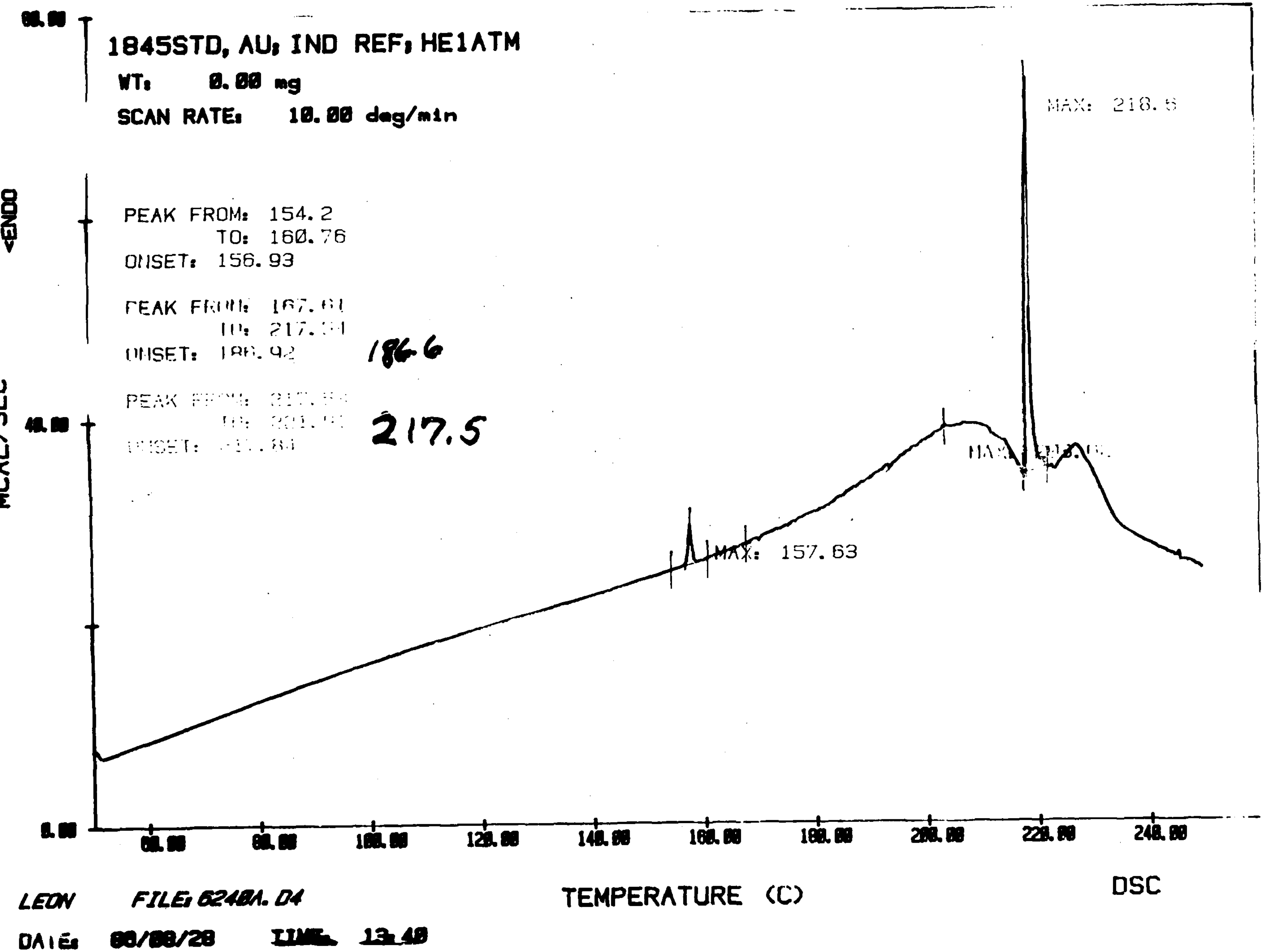
PERKIN-ELMER DSC HEAD AS MODIFIED FOR HIGH PRESSURE (1000 PSIG)

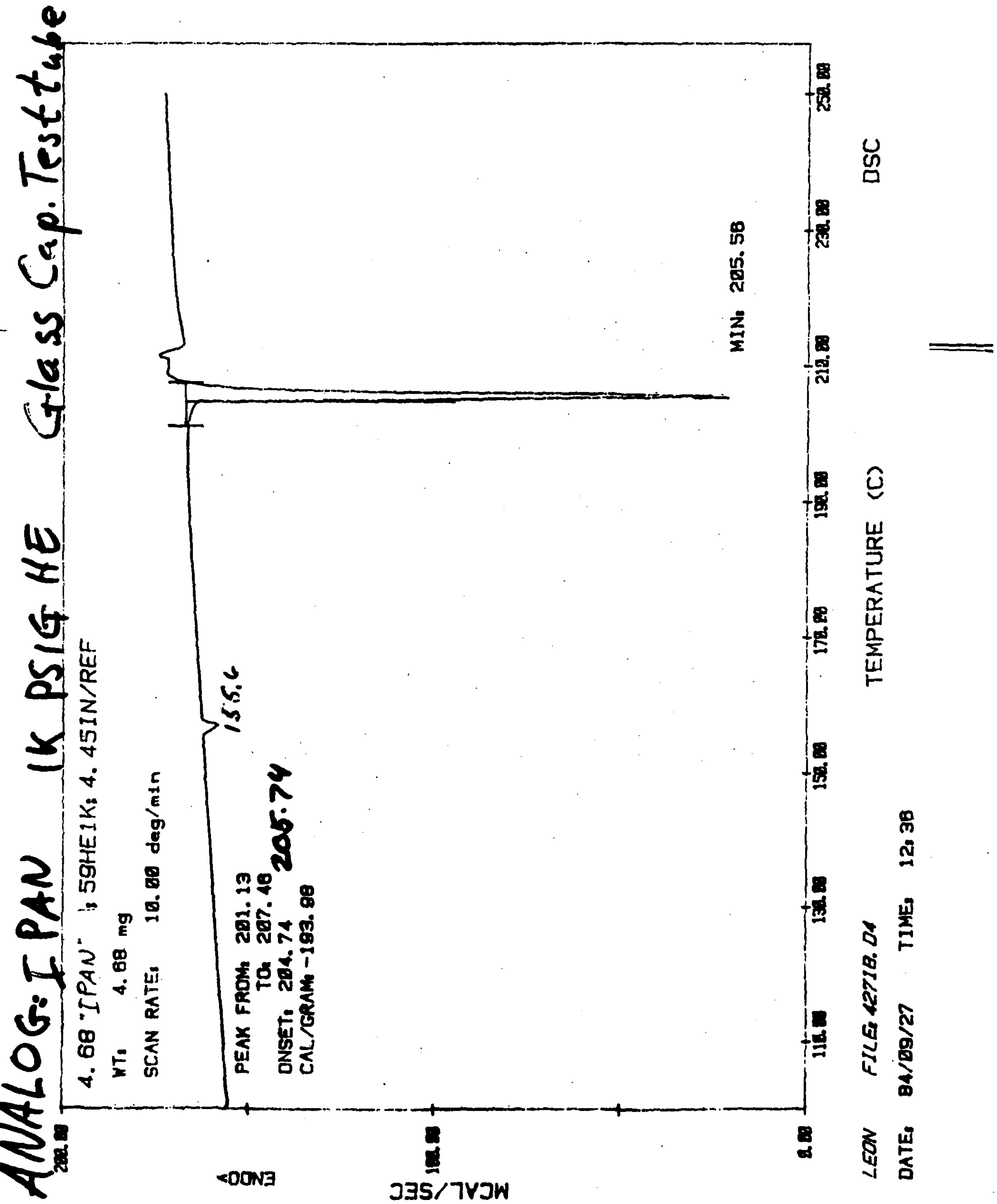



Horizontal capillary test tube
3.89CNTRL; 1KPSIG HE
WT: 3.89 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 184.83
ONSET: 198.64
CAL/GRAM: -131.86
195.9
159.3C
MIN: 199.54
ENDO>
MCAL/SEC
TEMPERATURE (C)
DSC
LEON FILE: 5025A.D4
DATE: 85/01/25 TIME: 08:17

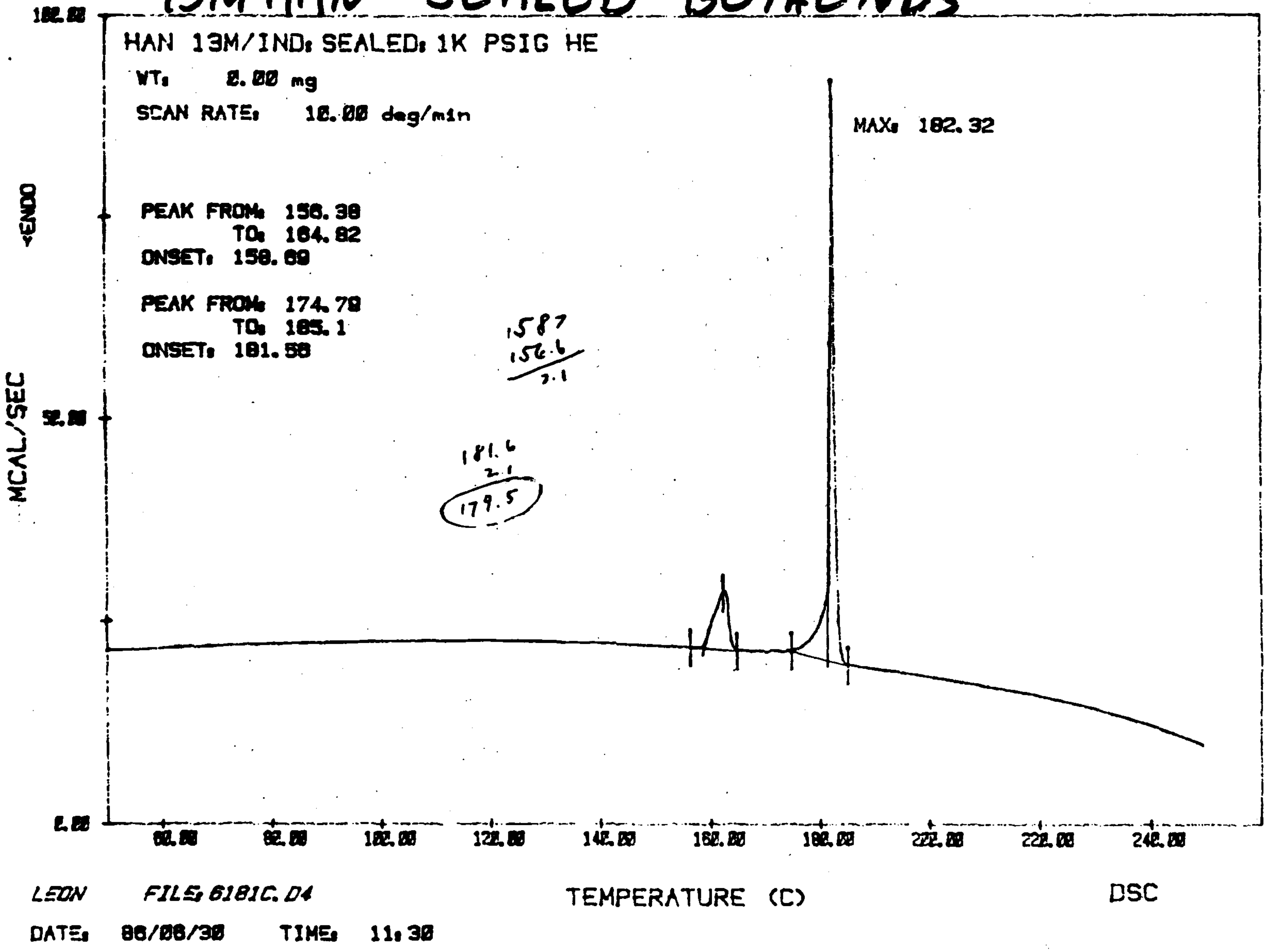

Gold Pan 1000 PSIG He
3.57 1845E244, 2.31 IN, 1K HE, AU
WT: 3.57 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 182.49
TO: 186.24
ONSET: 185.21
CAL/GRAM: -115
184.42
PEAK FROM: 157.23
TO: 159.26
ONSET: 157.42
MAX: 185.71
MAX: 158.16
150.00
75.00
0.00
<ENDO
MCAL/SEC
110.00
120.00
130.00
140.00
150.00
160.00
170.00
180.00
190.00
200.00
TEMPERATURE (C)
DSC
LEON FILE: 51928.D4
DATE: 85/07/11 TIME: 15:47

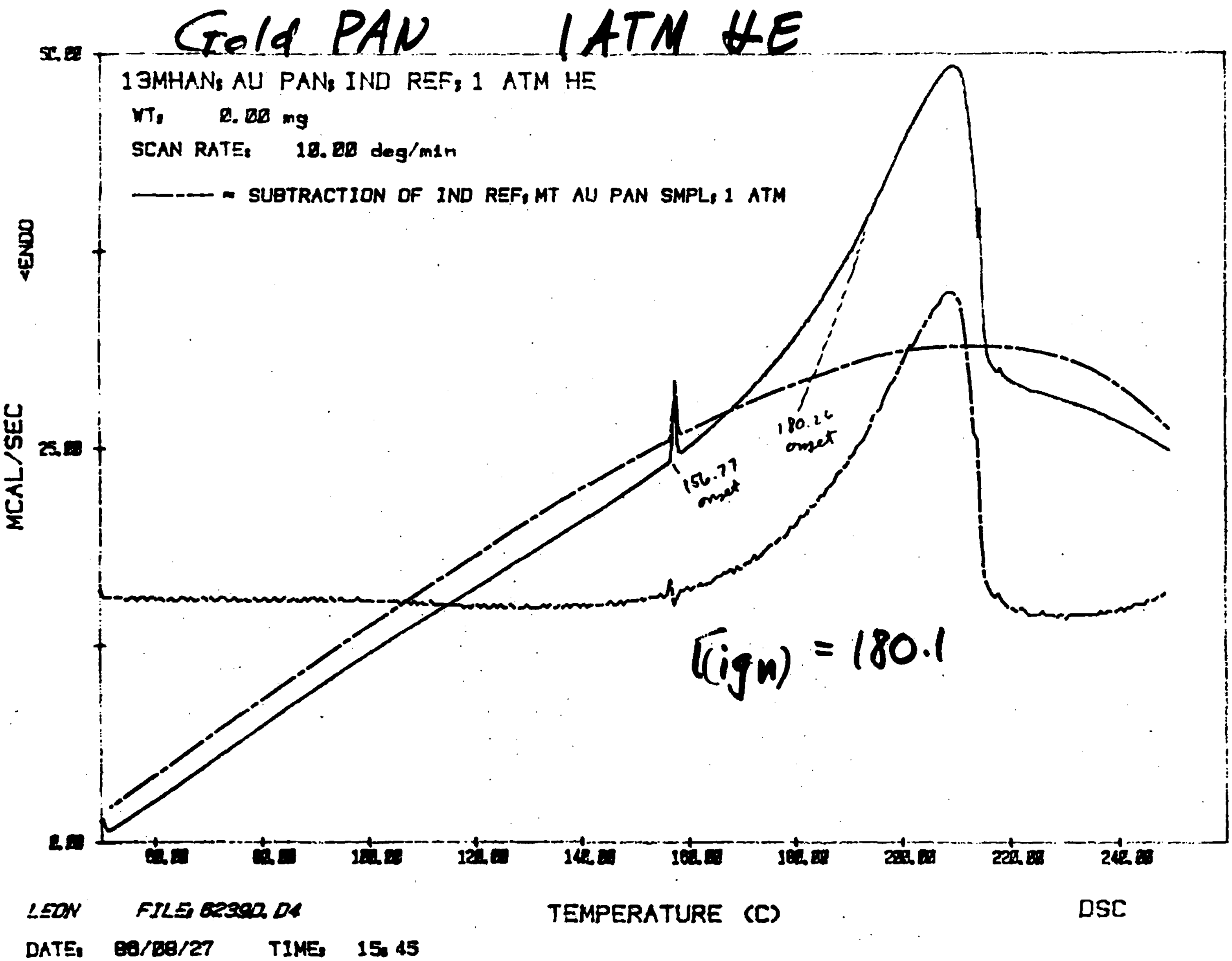

1845STD, AU; IND REF; HE1ATM
WT: 0.00 mg
SCAN RATE: 10.00 deg/min
= BASELINE FOR 6240A
<ENDO
MCAL/SEC
80.00
40.00
0.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
TEMPERATURE (C)
DSC
LEON
FILE: 6240A. D4
DATE: 80/08/20
TIME: 13:40

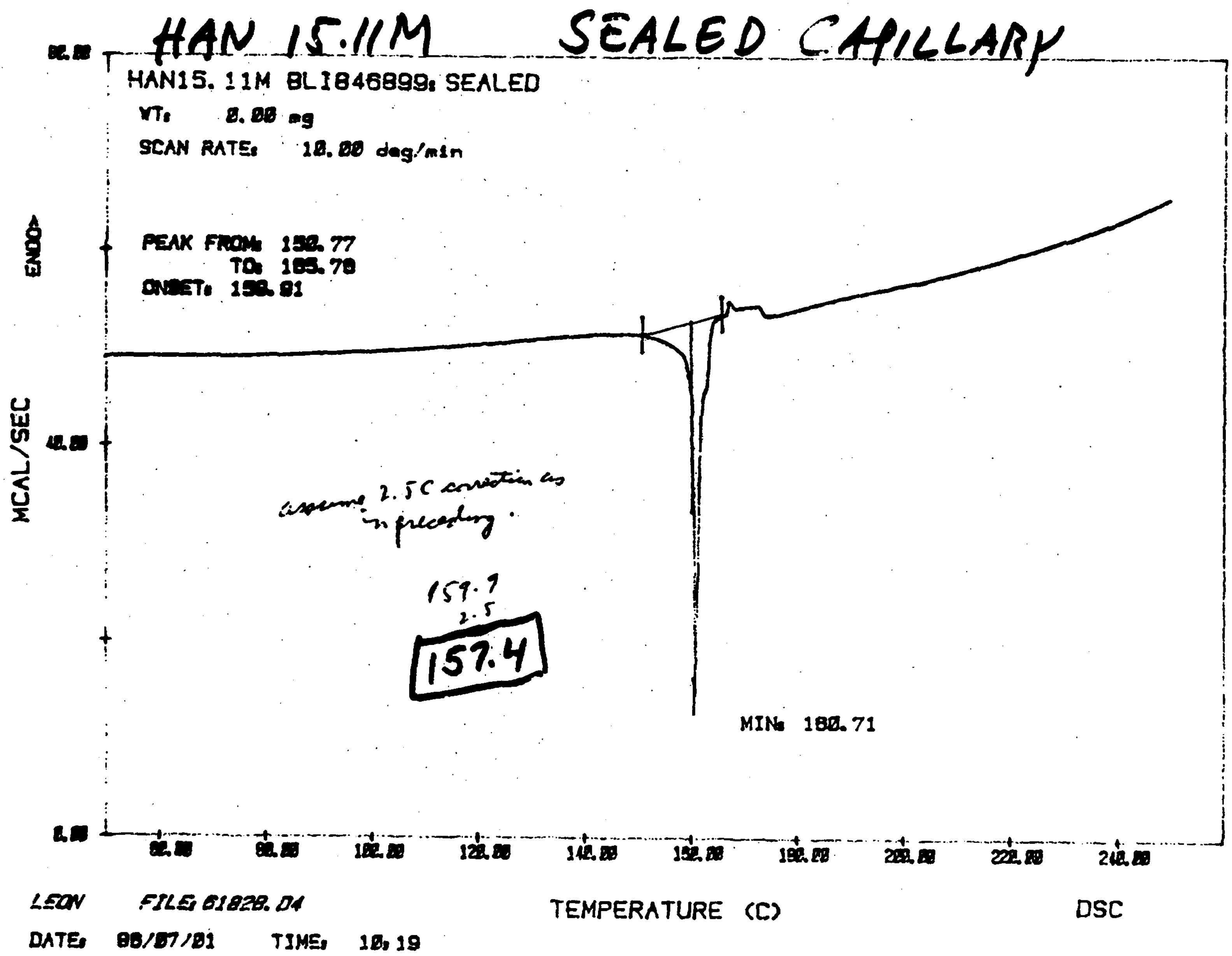

1845STD, AU; IND REF; HE1ATM
WT: 0.00 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 154.2
TO: 160.76
ONSET: 156.93
186.6
217.5
MAX: 157.63
MAX: 218.6
<ENDO
MCAL/SEC
80.00
40.00
0.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
TEMPERATURE (C)
DSC
LEON
FILE: 6240A.D4
DATE: 88/08/28
TIME: 13:40

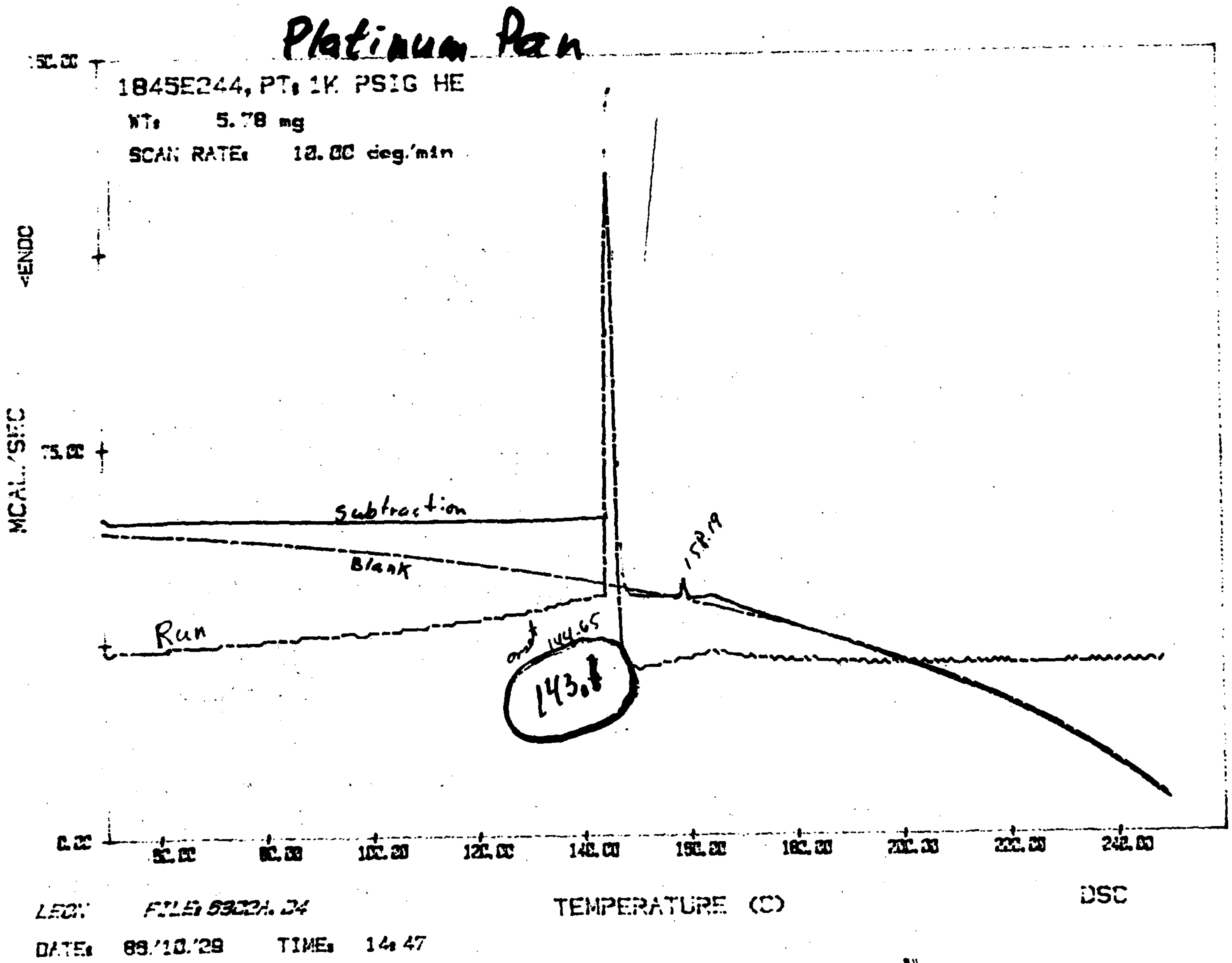

ANALOG: I PAN 1K PSIG HE Glass Cap. Testtube
4.68 'IPAN' ; 59HE1K; 4.45IN/REF
WT: 4.68 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 201.13
TO: 207.46
ONSET: 204.74
CAL/GRAM: -193.98
205.74
155.6
MIN: 205.58
200.00
100.00
0.00
MCAL/SEC
ENDO>
110.00
130.00
150.00
170.00
190.00
210.00
230.00
250.00
TEMPERATURE (C)
DSC
LEON
FILE: 4271B.D4
DATE: 84/09/27 TIME: 12:36

CAPILLARY
13M HAN SEALED BOTH ENDS




Gold PAN 1ATM HE
13MHAN; AU PAN; IND REF; 1 ATM HE
WT: 0.00 mg
SCAN RATE: 10.00 deg/min
—·—·— = SUBTRACTION OF IND REF; MT AU PAN SMPL; 1 ATM
<ENDO
MCAL/SEC
50.00
25.00
0.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
156.77 onset
180.26 onset
T(ign) = 180.1
TEMPERATURE (C)
DSC
LEON FILE: 82390.D4
DATE: 88/08/27 TIME: 15:45


HAN 15.11M SEALED CAPILLARY
HAN15.11M BL1846899: SEALED
WT: 0.00 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 150.77
TO: 165.78
ONSET: 159.91
ENDO>
MCAL/SEC
80.00
40.00
0.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
assume 2.5C correction as in preceding.
159.9
2.5
157.4
MIN: 160.71
LEON FILE: 61828.D4
DATE: 08/07/81 TIME: 10:19
TEMPERATURE (C)
DSC


Platinum Pan
1845E244, PT; 1K PSIG HE
WT: 5.78 mg
SCAN RATE: 10.00 deg/min
ENDO
MCAL/SEC
75.00
0.00
Subtraction
Blank
Run
158.19
onset 144.65
143.7
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
TEMPERATURE (C)
DSC
FILE 5302A.34
DATE: 88/10/29
TIME: 14:47

QUENCHED PRIOR TO INITIATION

13.24 M HAN IN GOLD PANS 1 ATM HE QUENCHED AT 150C
WEIGHT LOSS CORRESPONDS TO 100% OF WATER

1845 STANDARD IN HORIZONTAL GLASS CAPILLARIES
QUENCHED AT 190C
WEIGHT LOSS CORRESPONDS TO 47% OF WATER

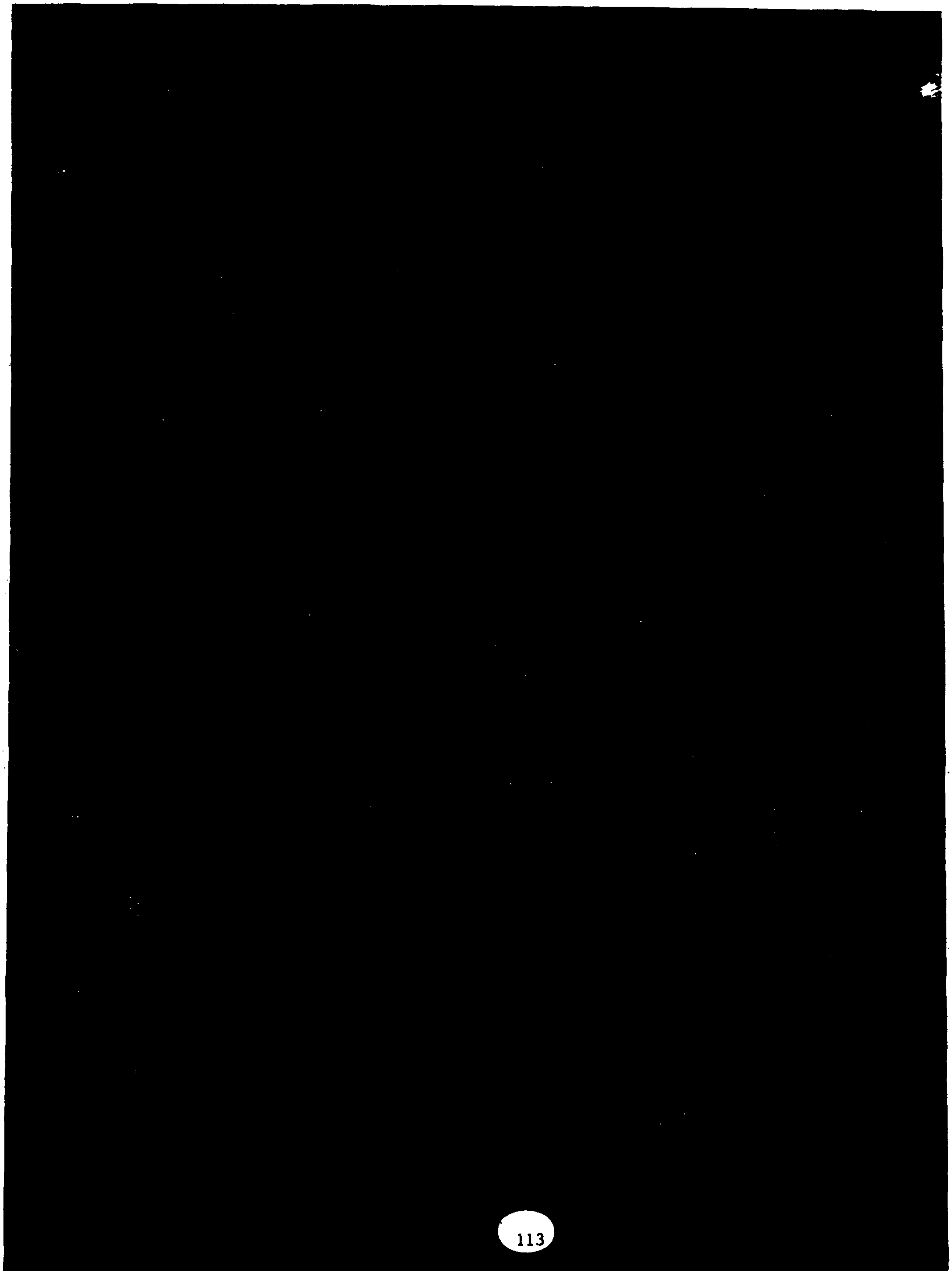
1845 STANDARD IN VERTICAL GLASS CAPILLARIES
QUENCHED AT 165C
WEIGHT LOSS CORRESPONDS TO 70% OF WATER

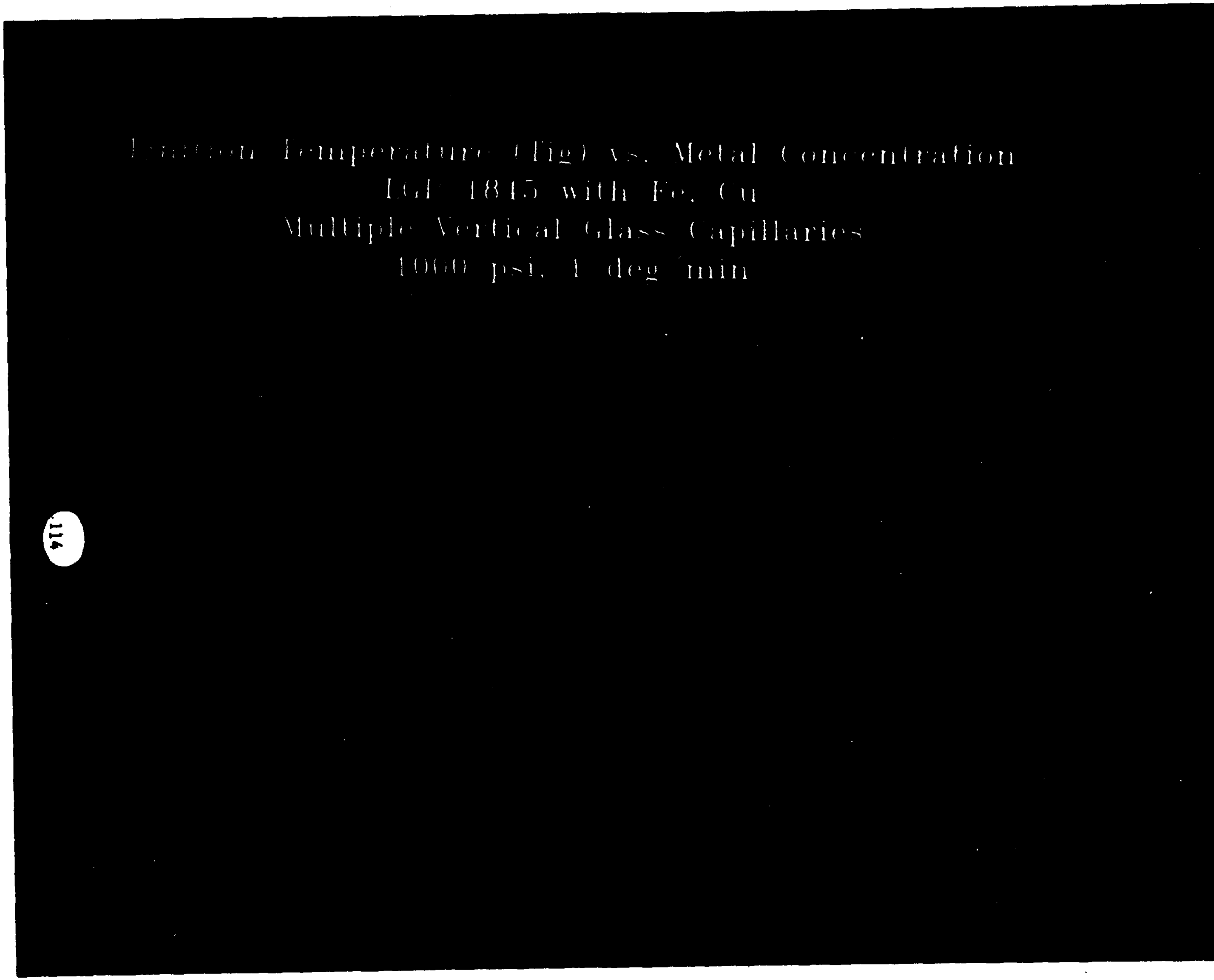
ADVANTAGES OF GLASS CAPILLARY TEST TUBES

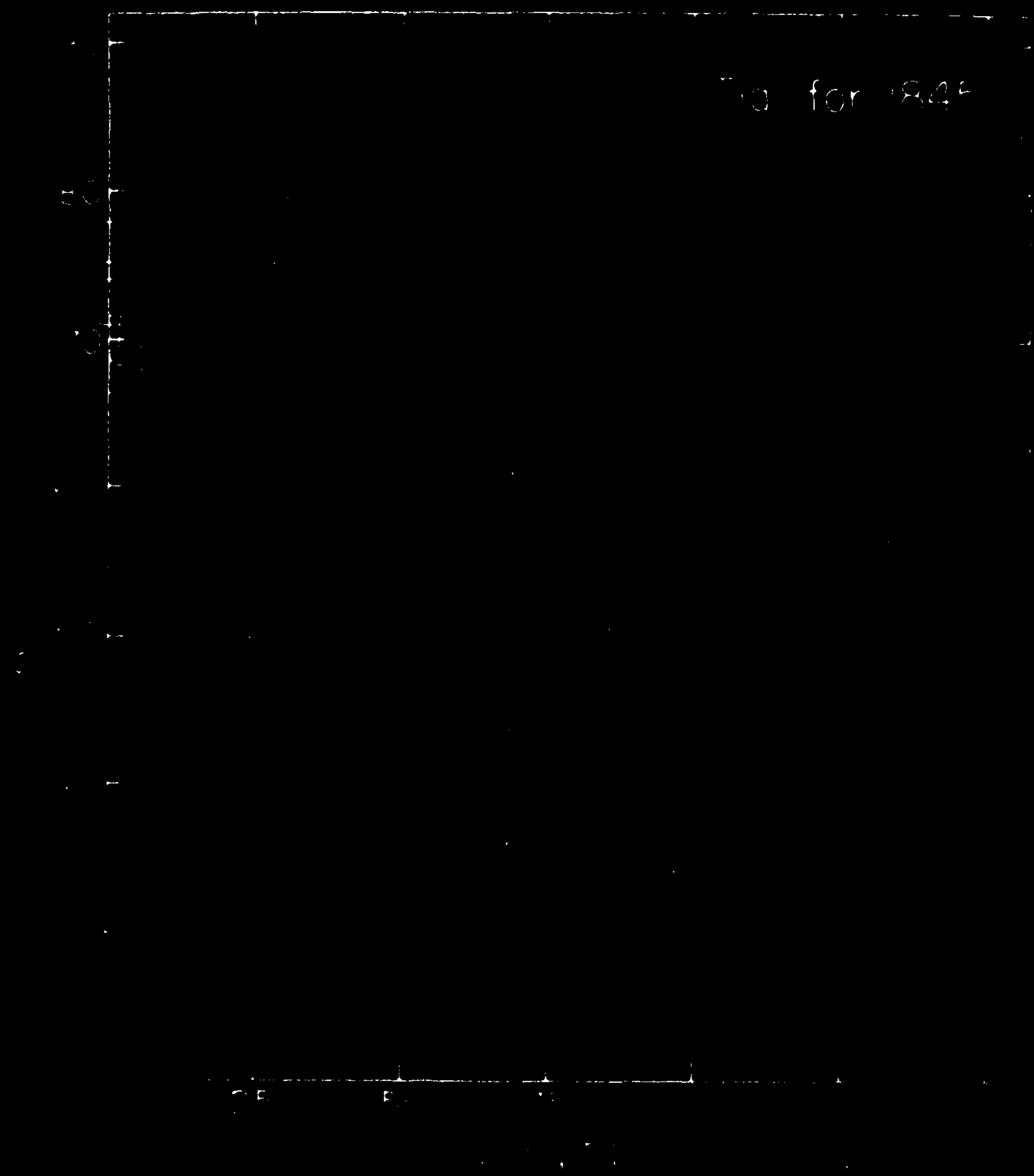
INERT

LOW SURFACE TO VOLUME RATIO

MULTIPLE SAMPLE CONFIGURATIONS POSSIBLE




Ignition Temperature (Tig) vs. Metal Concentration
LGF 1845 with Fe, Cu
Multiple Vertical Glass Capillaries
1000 psi, 1 deg/min



SUMMARY

SUPPRESSION OF WATER VAPORIZATION (PRESSURIZED DSC, LOW SURFACE TO VOLUME RATIO) RAISES T(ONSET)

LOW CONCENTRATIONS OF CU+2 AND FE+3 PRODUCE THE GREATEST DECREASE IN T(ONSET) PER UNIT METAL CONCENTRATION d(T)/dM

THE DESTABILIZING EFFECTS OF CU+2 AND FE+3 ARE OF EQUAL MAGNITUDE
(OBSERVABLE AT CONCENTRATIONS AS LOW AS 5 PPM)

DSC OF CRYSTALLINE HAN

TWO POLYMORPHS REPORTED

R.A. FIFER, "INFRARED SPECTRA AND POLYMORPHISM IN CRYSTALLINE HAN", 23RD JANNAF CONMBUSTION MEETING, CPIA PUB. 457,VOL III, P.159, OCTOBER, 1986

WHY?

CONTRIBUTES TO GENERAL BODY OF KNOWLEDGE

PROVIDES REFERENCE MATERIAL

PREPARATION OF HAN CRYSTALS

SUPERNATANT FLUID (MOTHER LIQUOR)
35, 50, 65C/VACUUM

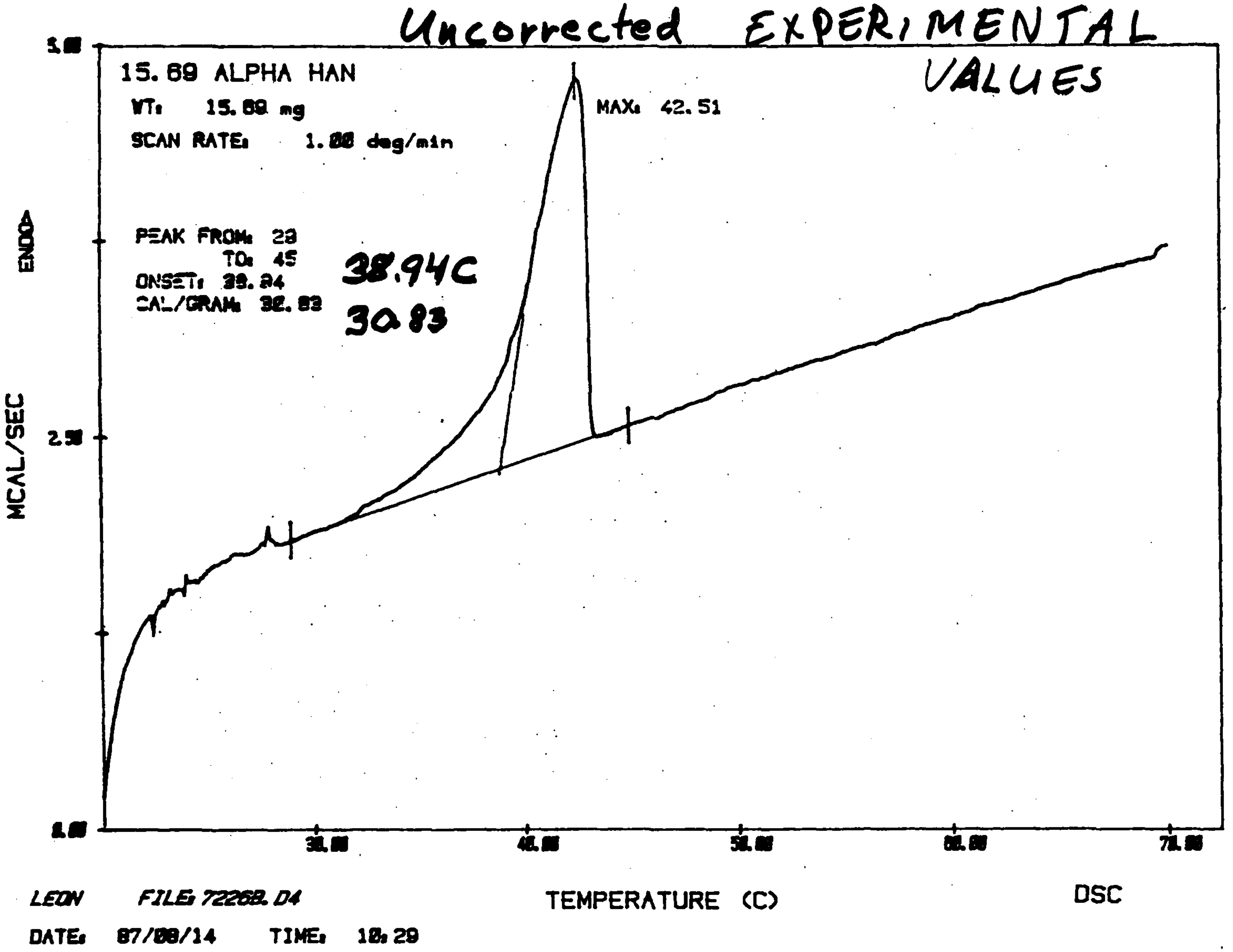
DRY BOX ATTACHMENT TO DSC

STORAGE OF MATERIAL BETWEEN RUNS

EXPERIMENTAL PROCEDURES

RESULTS

ONSET VARIED FROM 40C (35/VAC/DAYS) TO 36C (65/VAC/18HRS)
LATENT HEAT OF FUSION VARIED FROM 40 (35/VAC/DAYS) TO 27 CAL/GM (65/VAC/18HRS)

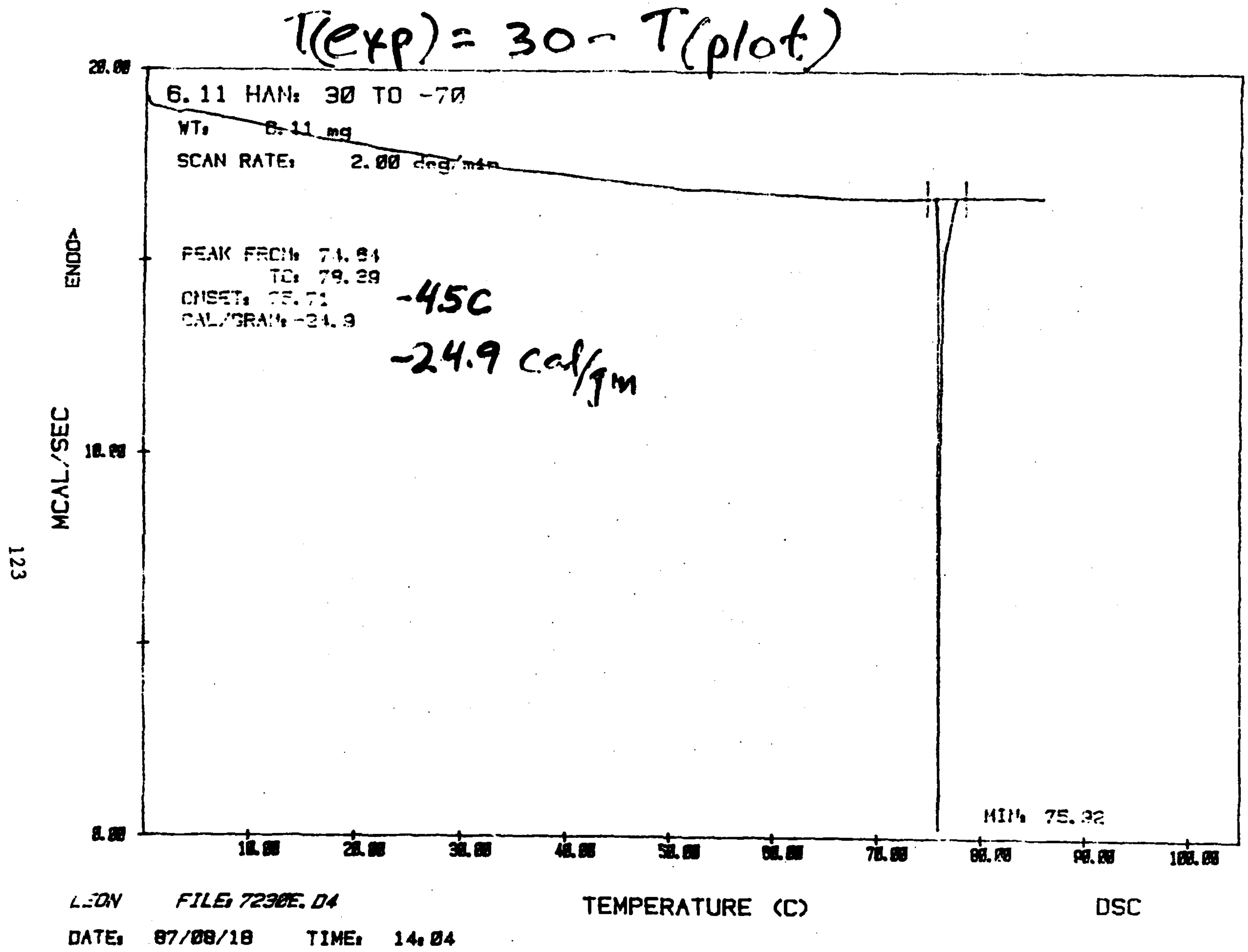

Uncorrected EXPERIMENTAL VALUES
15.69 ALPHA HAN
WT: 15.69 mg
SCAN RATE: 1.00 deg/min
PEAK FROM: 23
TO: 45
ONSET: 39.04
CAL/GRAM: 32.83
38.94C
30.83
MAX: 42.51
ENDO>
MCAL/SEC
5.00
2.50
0.00
30.00
40.00
50.00
60.00
70.00
TEMPERATURE (C)
DSC
LEON
FILE: 72268.D4
DATE: 87/08/14
TIME: 10:29

ALPHA HAN: LATENT HEAT OF FUSION

RUN ID	ONSET	CAL/GM	C/MIN	THERMAL RANGE
7230F	35.89C	25.60	+2	−30 TO +70C
7230D	36.21C	29.33	+1	+20 TO +70C
7229B	34.76C	24.95	+2	+20 TO +70C
7231D	36.00C	36.00	+2	+20 TO +70C

CORRECTED VALUES

ONSET = 35.72 ± 0.65 CAL/GM = 26.97 ± 2.05


T(exp) = 30 - T(plot)
6.11 HAN: 30 TO -70
WT: 6.11 mg
SCAN RATE: 2.00 deg/min
PEAK FROM: 74.84
TO: 79.29
-45C
-24.9 cal/gm
MIN: 75.32
ENDO>
MCAL/SEC
20.00
10.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
TEMPERATURE (C)
DSC
FILE: 7230E.D4
DATE: 87/08/18
TIME: 14:04

BETA HAN: HEAT RELEASED DURING CRYSTALLIZATION

RUN ID	ONSET	CAL/GM	C/MIN	THERMAL RANGE
7230G	-47.37C	-27.38	-2	0 TO -70C
7230E	-46.81C	-24.97	-2	+30 TO -70C
7229F	-46.38C	-26.06	-2	+30 TO -70C
7229E	-47.46	-29.55	-2	+30 TO -70C
7229D	-50.65	-25.65	-2	+30 TO -70C

ONSET = -47.73 ± 1.69 CAL/GM = -26.72 ± 1.81

INDICATIONS ARE THAT THE ALPHA AND BETA FORMS HAVE EQUAL OR NEARLY EQUAL (WITHIN EXPERIMENTAL LIMITS) LATENT HEATS OF FUSION

FURTHER CHARACTERIZATION OF THE CRYSTALS BEING STUDIED ARE NECESSARY

CONCLUSIONS

WOULD BE NICE, BUT WOULD YOU SETTLE FOR SOME QUESTIONS?

FUTURE WORK

CHARACTERIZE CRYSTALLINE FORMS SPECTROSCOPICALLY

RUN BOTH FORMS THROUGH PROGRAMMED TEMP INCREASE TO OBTAIN APPROPRIATE T(ONSET) AND LATENT HEAT OF FUSION

PROGRAM LIQUID THROUGH TEMP DECREASE TO CRYSTALLIZATION, THEN CHARACTERIZE THE CRYSTAL SPECTROSCOPICALLY

OBSERVE STORED CRYSTALS TO DETERMINE IF THE TWO FORMS ARE INTERCONVERTIBLE, EITHER PARTIALLY OR TOTALLY

OBSERVE STORED CRYSTALS FOR POSSIBLE DETERIORATION
EVOLVED GASES, WATER FORMATION, CHANGES IN HEAT OF FUSION, MELTING TEMPERATURE, IGNITION TEMPERATURE

Fast Thermal Decomposition of Liquid Propellant 1845

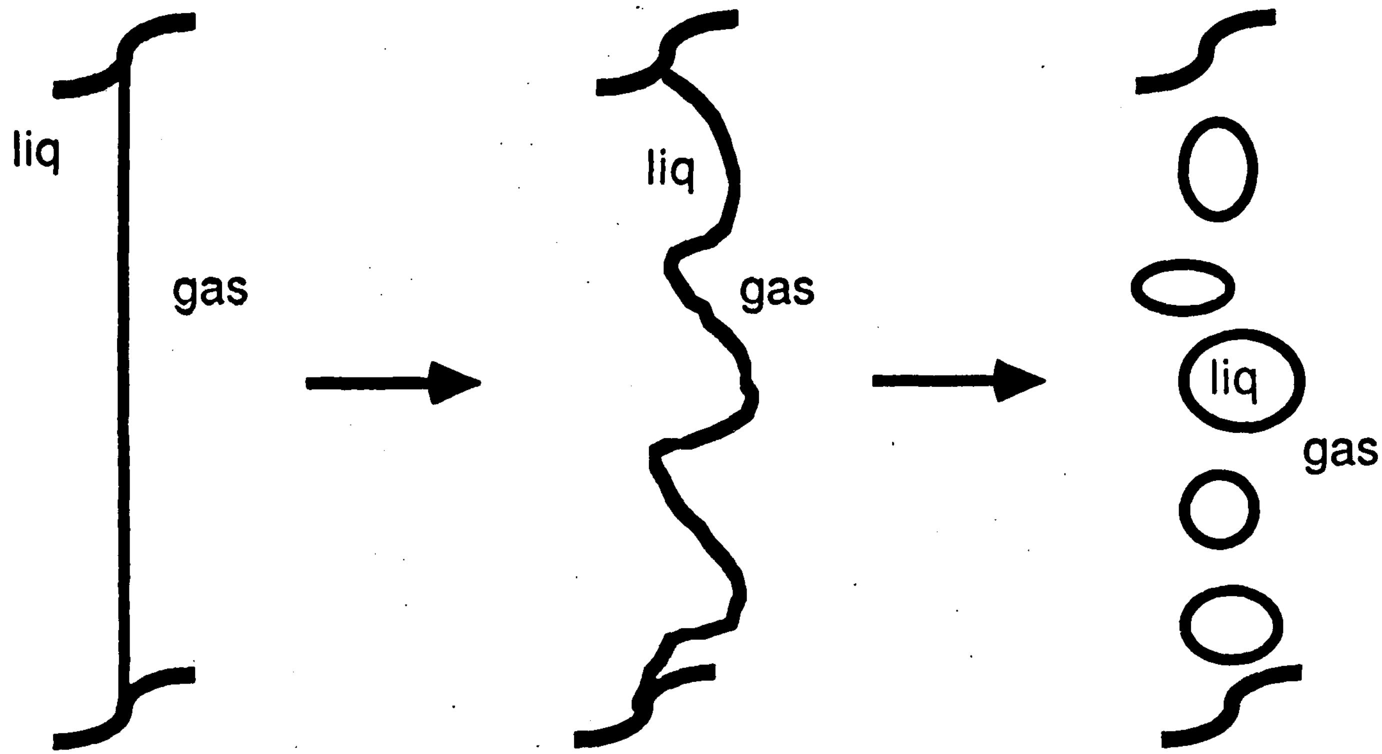
J.T. Cronin, T.B. Brill. Department of Chemistry
University of Delaware, Newark, DE 19716

The high rate (>100^{o}C/sec) decomposition charateristics of liquid propellant LP1845 will be described with the rapid-scan FTIR/thermal profiling technique. The decomposition characteristics of HAN and TEAN were examined and then compared to the pyrolysis behavior of LP1845. A five step process that describes the major events occurring during the fast thermal decomposition/ignition of LP1845 will be presented. A progress report on the acoustic levitation project will be presented.

Stability Characteristics of Deflagrating Liquid Propellants

Rob Armstrong
and
Steve Vosen
Combustion Research Facility
Sandia Labs, Livermore 94550

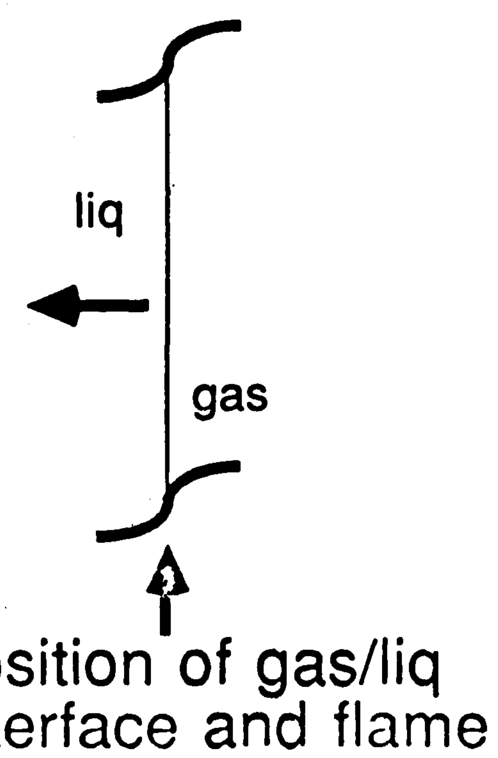
Why stability?



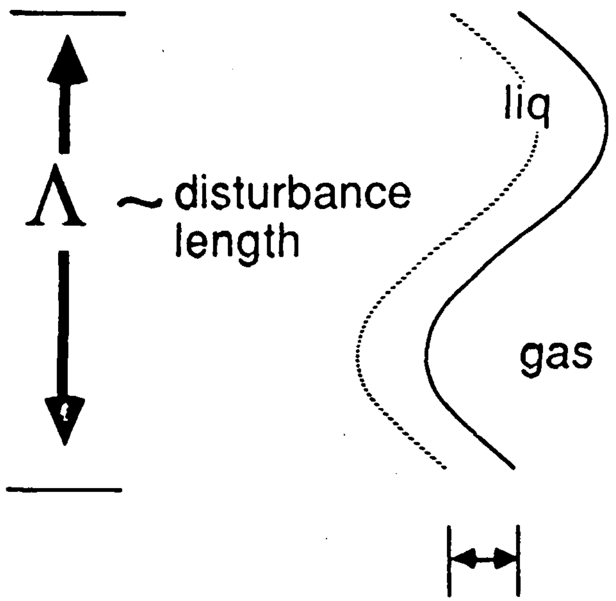
shows the length scale of fluid-mechanical breakup (droplet size)

Initial state from which stability is determined

- steady, planar burning



Previous investigations



λ ~ thermal-diffusive distance $\approx 10\mu - 1\mu$

- Landau (1944), Zeldovich (1980)
- Frankel & Shivashinsky (1982), Pelce & Clavin (1982) Matalon & Matkowsky (1982)

$$\omega = \omega_1 (\lambda/\Lambda) + \omega_2 (\lambda/\Lambda)^2 + \ldots$$

(disp. rel'n)

- to this approximation there is no contribution from viscous forces, diffusive forces have stabilizing influence
- smallest wave numbers (largest length disturbance) are always unstable

Experimental evidence

- it is clear that the small wave number disturbances are observed

- S. Vosen has evidence for a "fog" of small ($10\mu - 1\mu$) droplets also

<u>physical origin?</u>

- impossible for fluid mechanical turbulence to be responsible

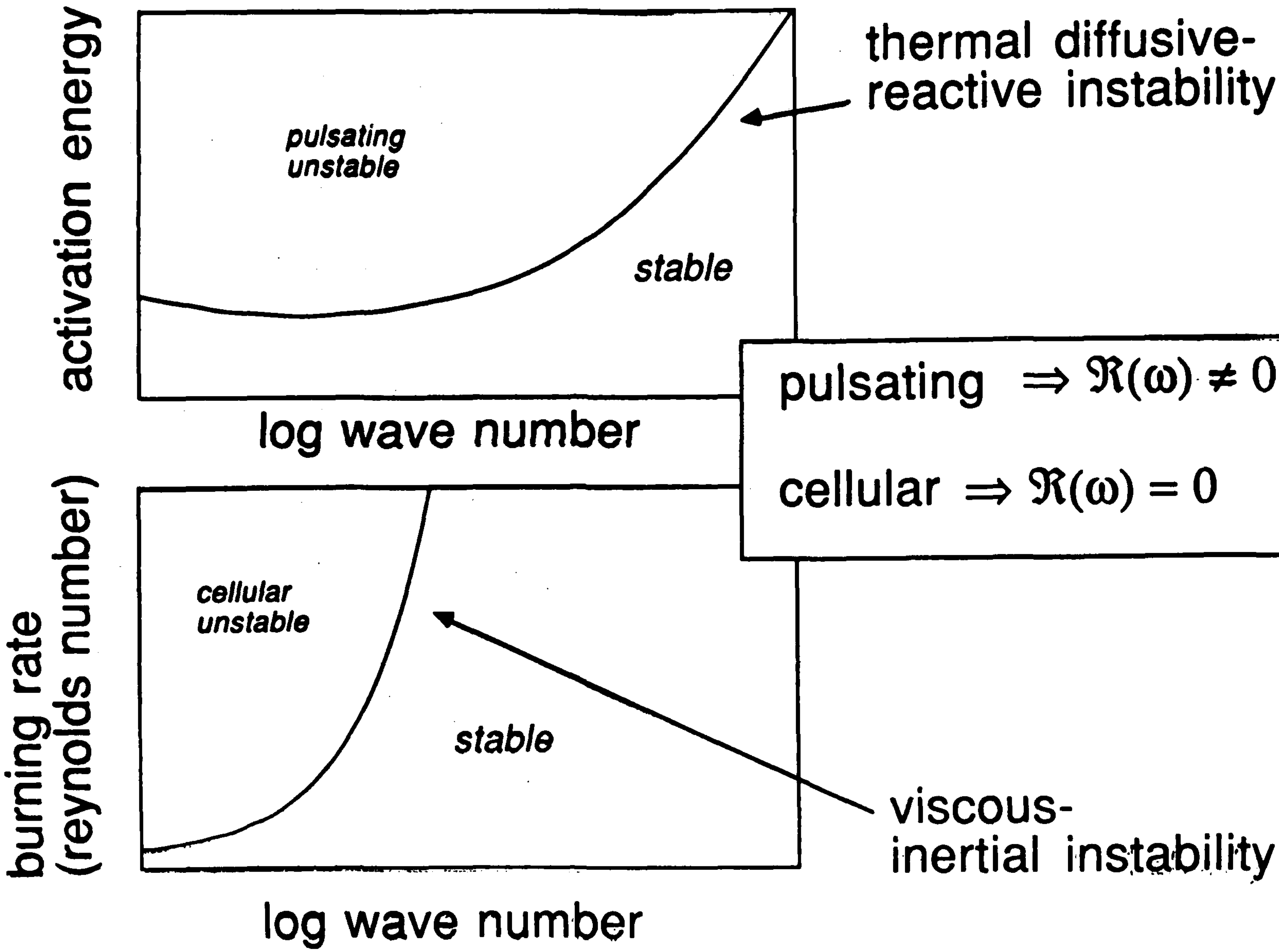
- is on the correct length scale over which thermal - diffusive processes are active

Experimental evidence (cont'd)

possible mechanisms:

- thermal-diffusive, reactive interaction
  (known to exist for solid propellants)
- thermal-diffusive, surface tension gradient interaction
- thermal-diffusive, homogeneous shear

Two length scale problem



pulsating $\Rightarrow \Re(\omega) \neq 0$

cellular $\Rightarrow \Re(\omega) = 0$

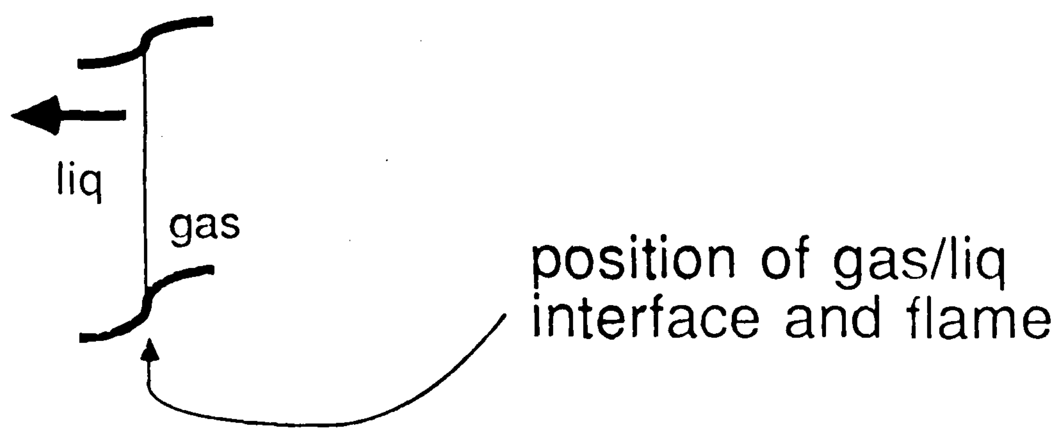
Combine the two in a way relevant to liquid prop. combustion

- do not wish to use a perturbative approach that is asymptotic to either the thermal or inertial length scales
- would like to treat all of these forces as equals
- as a result a very large system must be dealt with (which is the reason for the asymptotic approach in the first place)
- we have used advanced techniques to accomplish the solution in the same analytic way as a human would do "by hand"

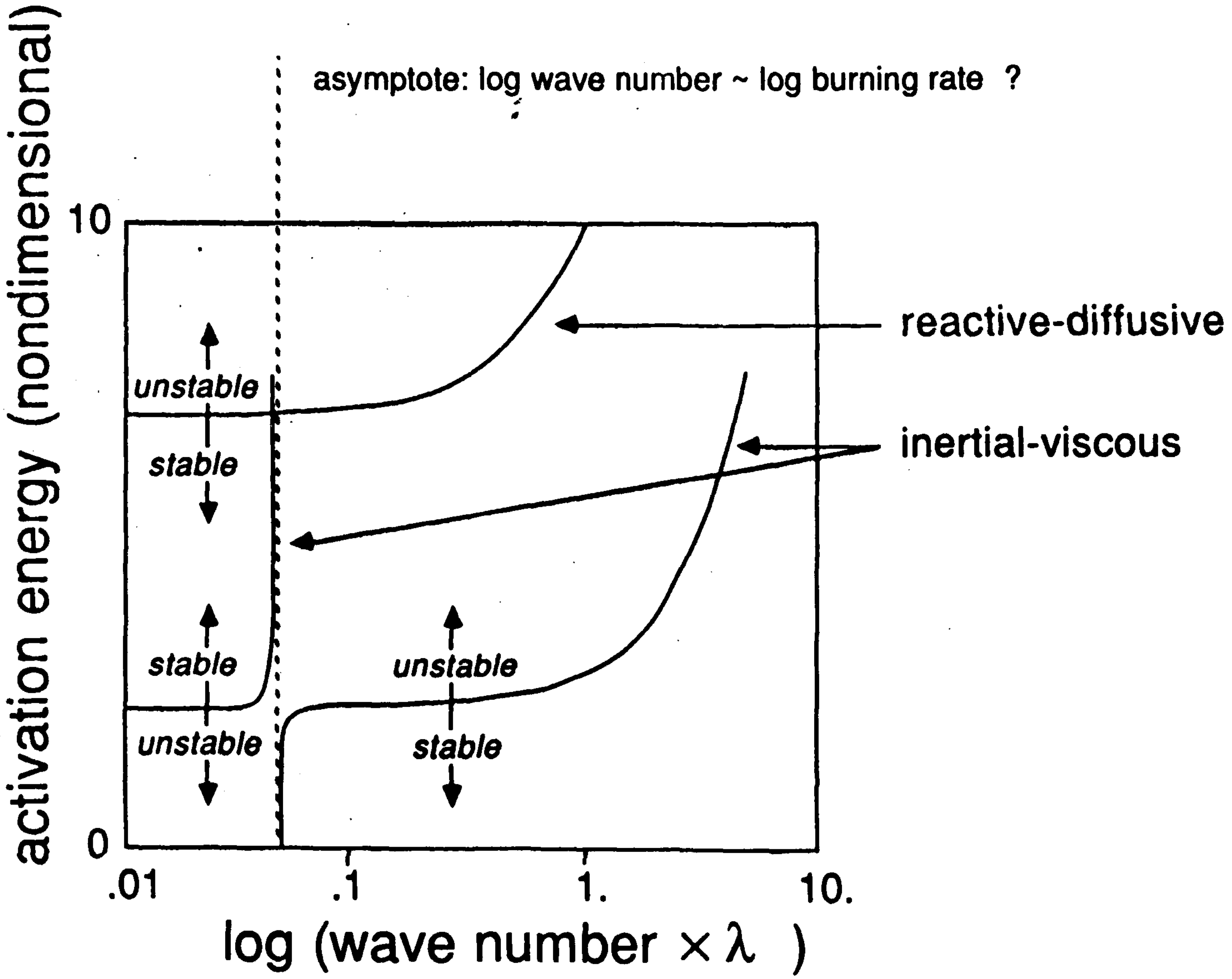
— disadvantage is that the system must be couched in general fashion
— takes the form of a linear operator in fourier - laplace whose determinant forms the dispersion relation

Model system

- flame is at the gas/liq interface
- rate of reaction has Arrhenius kinetics
- include full transport (fluid-thermal) and surface tension
- does not require a " λ/Λ " series expansion, only assumes that the reaction zone is thin
- recognizes a large Lewis number in the liquid phase and a general "jump" in transport properties across the gas/liquid boundary



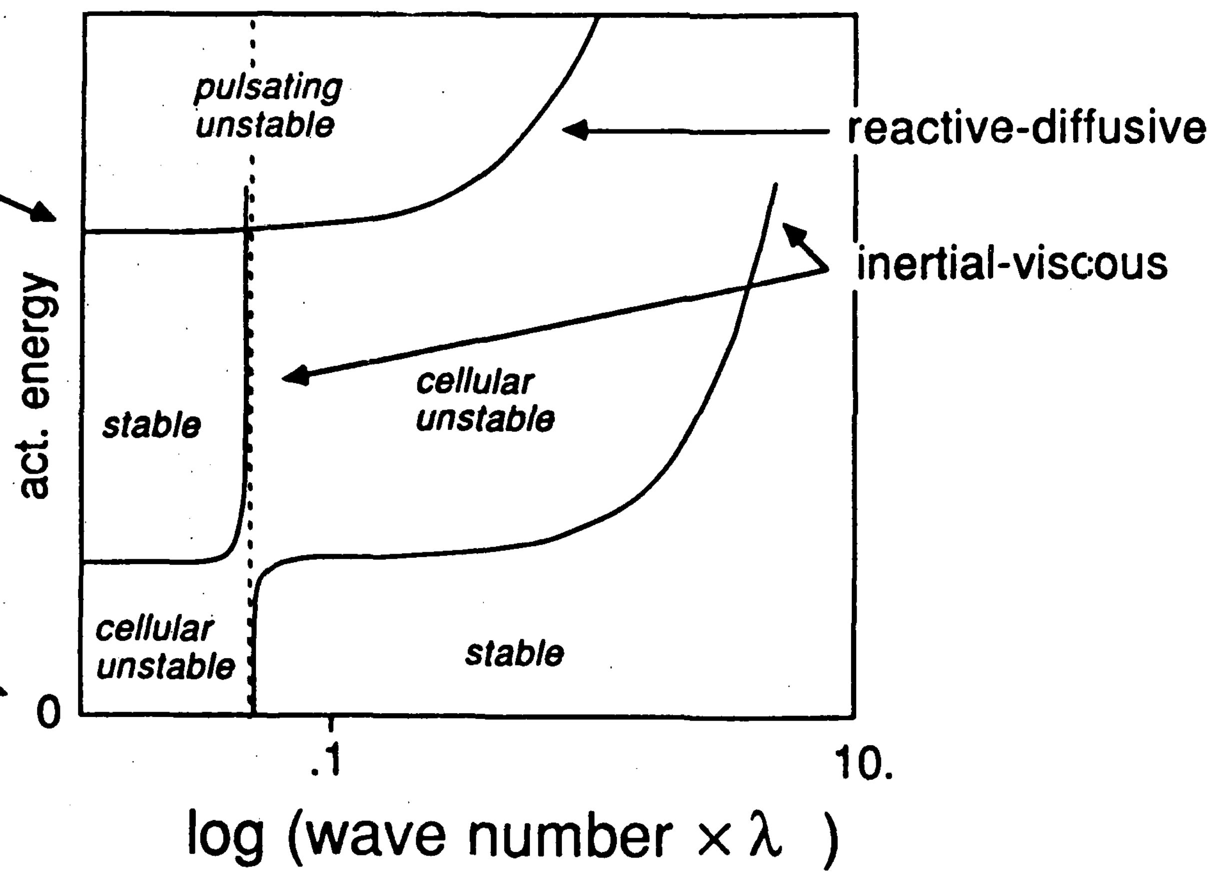
Results


asymptote: log wave number ~ log burning rate ?
reactive-diffusive
inertial-viscous
unstable
stable
stable
unstable
unstable
stable
activation energy (nondimensional)
10
0
.01
.1
1.
10.
log (wave number × λ)

More results

obtain the
solid reactive-
diffusive result
for liq Re —> 0

obtain the
Landau result
for act. energy =0
for wave
number —> 0
or for liq & gas
Re —> ∞



cellular $\Rightarrow \Re(\omega) = 0$ pulsating $\Rightarrow \Re(\omega) \neq 0$

Conclusion

<u>things done</u>

- formalism developed to enable the solution of this large system (including surface tension & gravity)
- found the stability map for liquid propellant model without gravity & surface tension
- have found the exact analytic asymptotic limit for same for wave number —> 0

<u>things to do</u>

- discover the nature of the singularity in the inertial-viscous stability boundary
- include surface tension and gravity
- better chemistry

Summary

- if wave number implies droplet size then this theory predicts that "fog-like" droplets can occur due to diffusive-reactive instability.
- the presence of small droplets is likely to modify burning rate of a secondary flame

THE COMBUSTION OF HYDROXYLAMMONIUM NITRATE BASED LIQUID PROPELLANTS *

Steven R. Vosen
Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94550

ABSTRACT

To better understand the physical processes which occur during the combustion of liquid propellants (LP), a strand burner was used to study hydroxylammonium nitrate based LP flames. By observing the combustion of LP in such an arrangement, much has been deduced of the physical processes that occur during LP ignition and combustion, at pressures which are relevant to LP gun ignition.

Combustion experiments were performed in which mixtures of the salts hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) in water were ignited by an electric discharge, in a pressure vessel at pressures of up to 34 MPa (5000 psi). Specifically, the mixtures discussed in this paper are the propellant designated as LP 1846 (60.8 % HAN, 19.2 % TEAN, and 20.0 % water by weight) and HAN/water mixtures. The mixtures were loaded into a container (strand burner) that had a 5 mm (0.20 inch) square cross section, was 40 mm (1.57 inch) deep, and was open on top. Electrodes in two sides of the burner allowed for a discharge through the mixtures, and quartz windows on the other sides allowed for observation of LP combustion. The burner was located in a pressure vessel with a volume (.013 m^3, 0.46 ft^3) large enough to ensure that only small changes in pressure occurred during combustion.

Images of the combustion were obtained through windows in the pressure vessel by backlit photography, and were recorded on a video system at a rate of 60 frames per second, with an exposure of 100 microseconds. These images clearly show the movement of a liquid-gas interface and a bright flame during LP combustion.

The following conclusions have been made based on photographs of LP and HAN/water combustion, samples of combustion residue in the combustion chamber, and the pressure in the chamber:

1) As reported by other experimenters, it has been confirmed that there is a decrease in the average volumetric burning rate of LP in the pressure range of 6.7 to 34 MPa (1000 to 5000 psi).

2) There are two regions in the LP flame where reactions occur: at the liquid-gas interface and above the liquid-gas interface.

* This work was supported by a memorandum of understanding between the Department of Energy and the Department of the Army.

3) For the pressure range studied, HAN decomposition governs the overall combustion rate of HAN-based propellants.

THE COMBUSTION OF HAN BASED LIQUID PROPELLANTS

STEVEN R.VOSEN

COMBUSTION RESEARCH FACILITY
SANDIA NATIONAL LABORATORIES
LIVERMORE, CALIFORNIA

Work supported by a Memorandum of Understanding
between Department of the Army and DOE

Approach

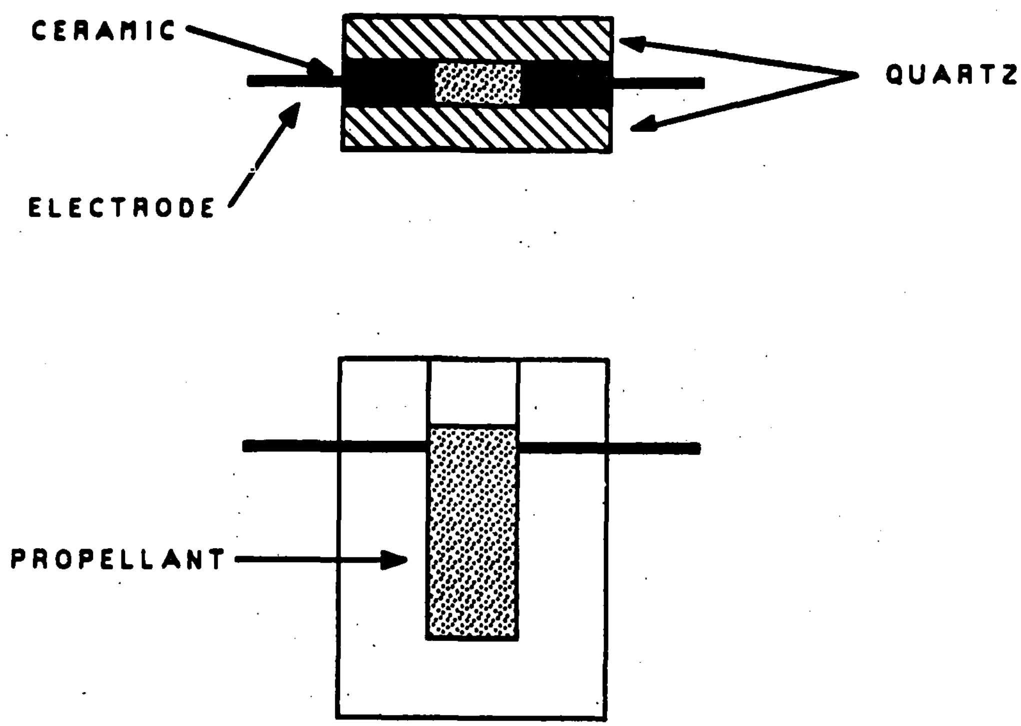
BURN LIQUID PROPELLANTS
IN A CONTROLLED ENVIRONMENT TO DETERMINE

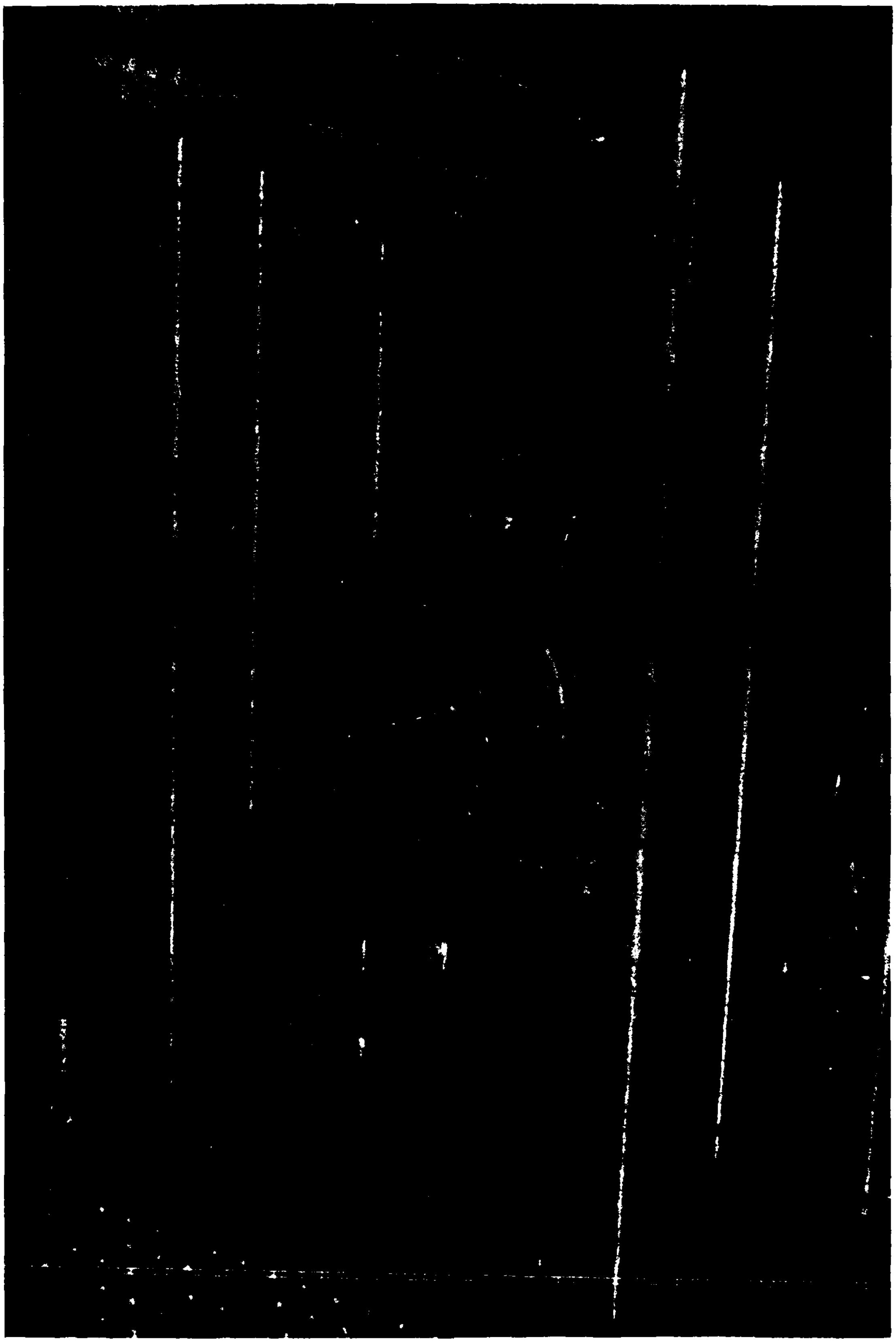
- Burning Rates
- Where Reactions Occur
- Importance of Two-Phase Region
- Flame Stability

Experimental Conditions

- Constant Pressure (1500 - 5000 psi)
- Burn a Column of Fluid (5 mm X 5 mm X 25 mm)
- Electric Discharge Ignition (20 J in 30 μsec)

Burner





The rate of combustion is given by:

$$\dot{m} = \rho_u S_u A_f$$

Flame area.

"LAMINAR Burning Speed"

S_u is a function of Chemistry

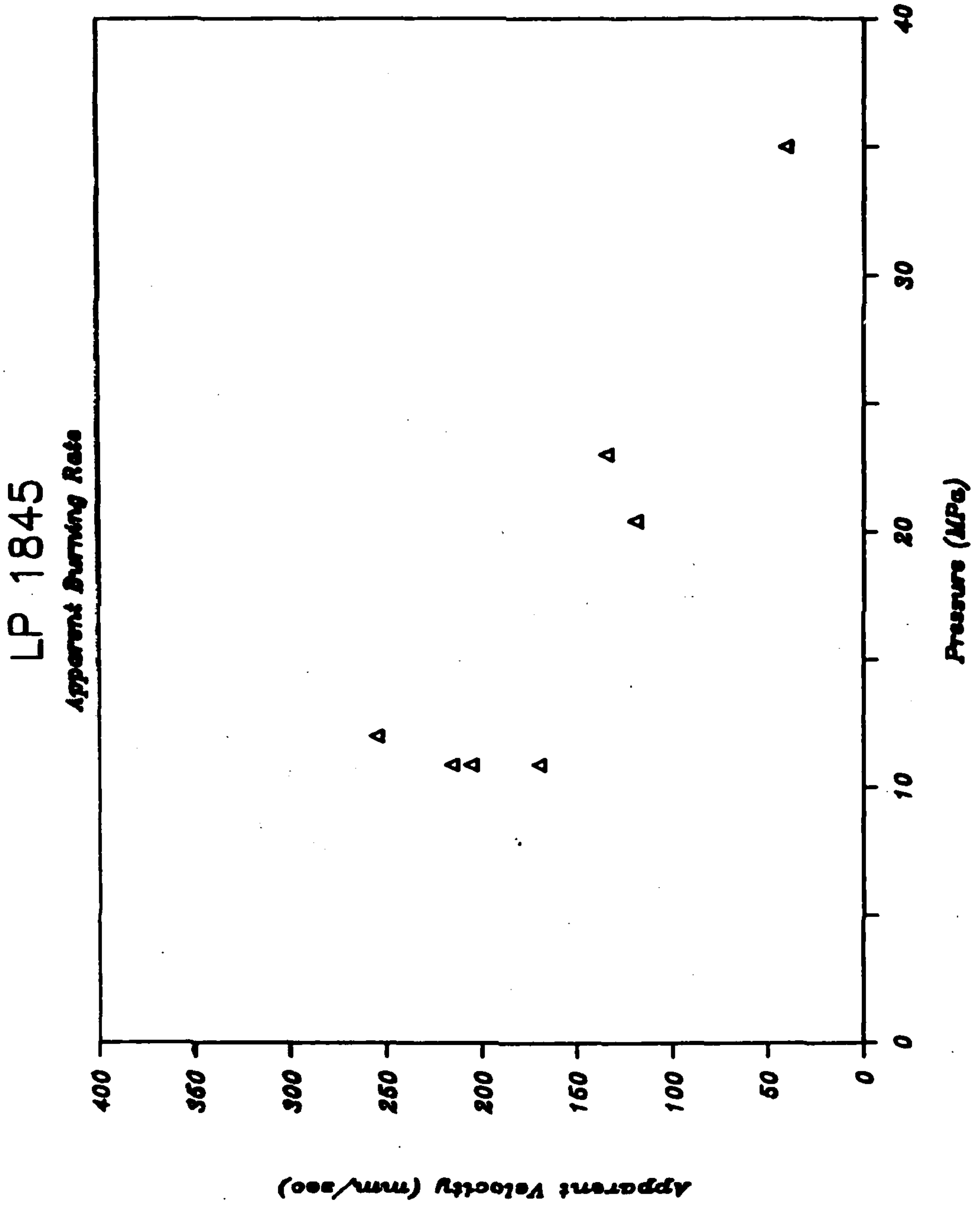
A_f is a function of:

1) Turbulence

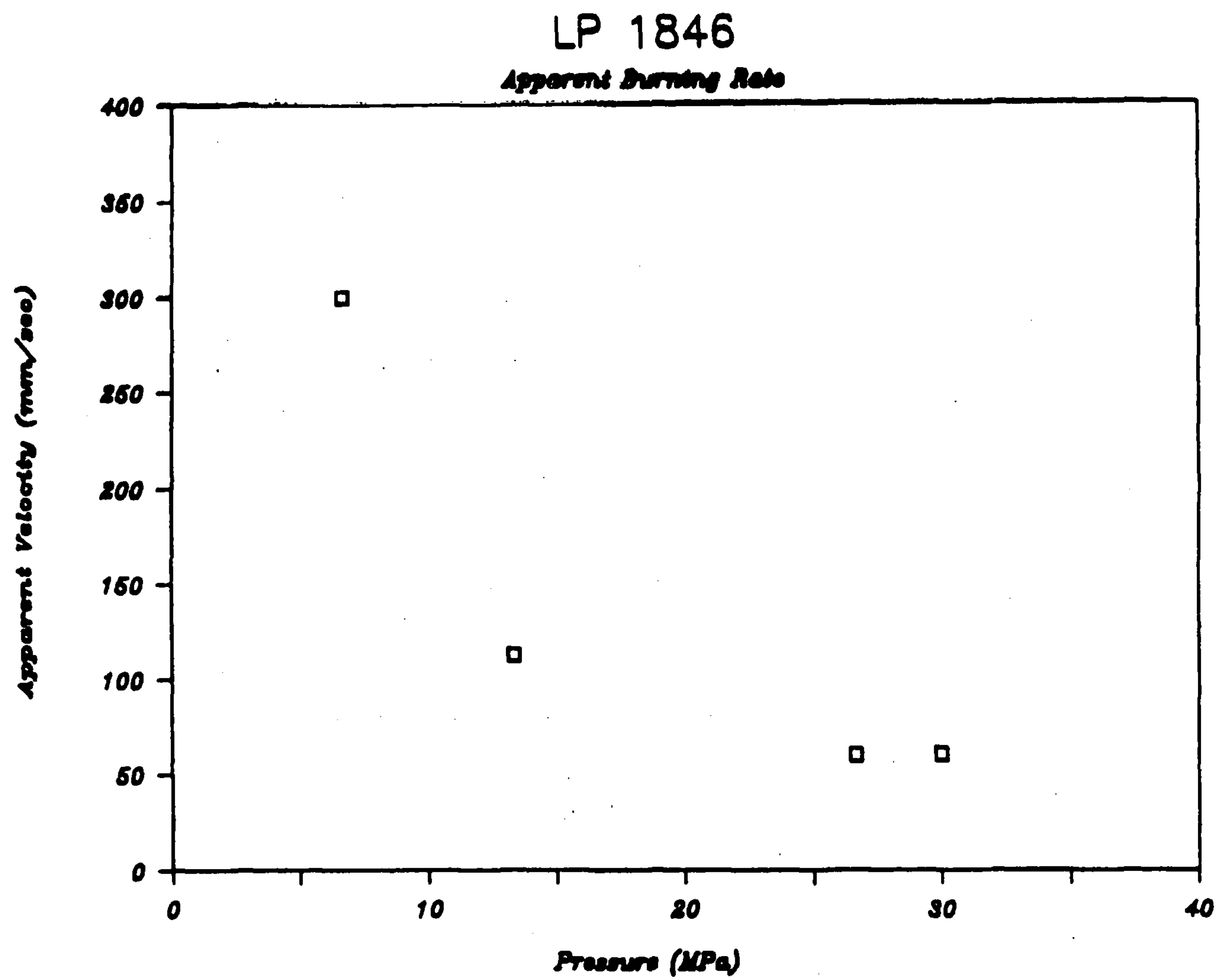
2) Instabilities

Observations

- Regression Rate Decreases with Pressure
- Two Zone Flame Structure
- Burning is Oscillatory



LP 1845
Apparent Burning Rate
Apparent Velocity (mm/sec)
Pressure (MPa)
0
10
20
30
40
0
50
100
150
200
250
300
350
400



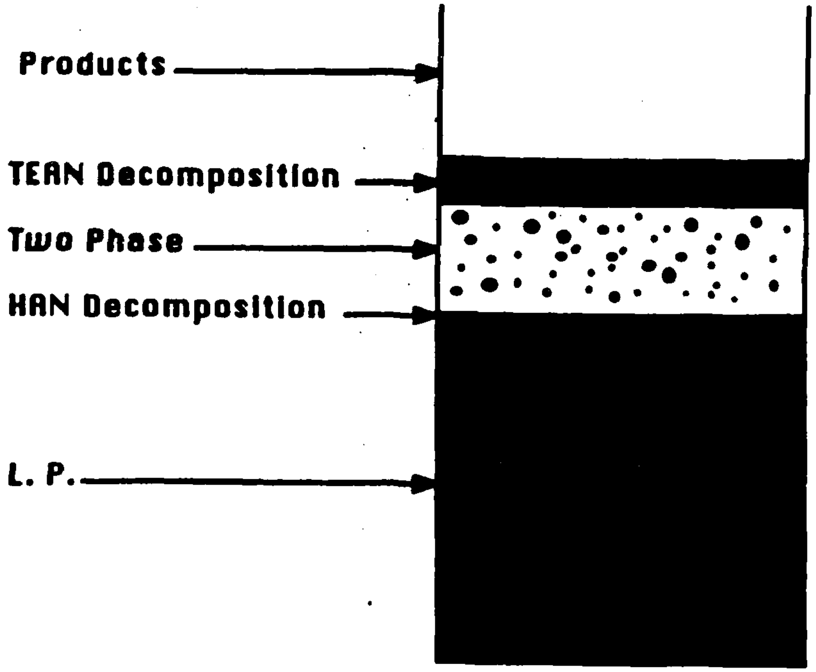
LP 1846
Apparent Burning Rate
Apparent Velocity (mm/sec)
400
350
300
250
200
150
100
50
0
0
10
20
30
40
Pressure (MPa)

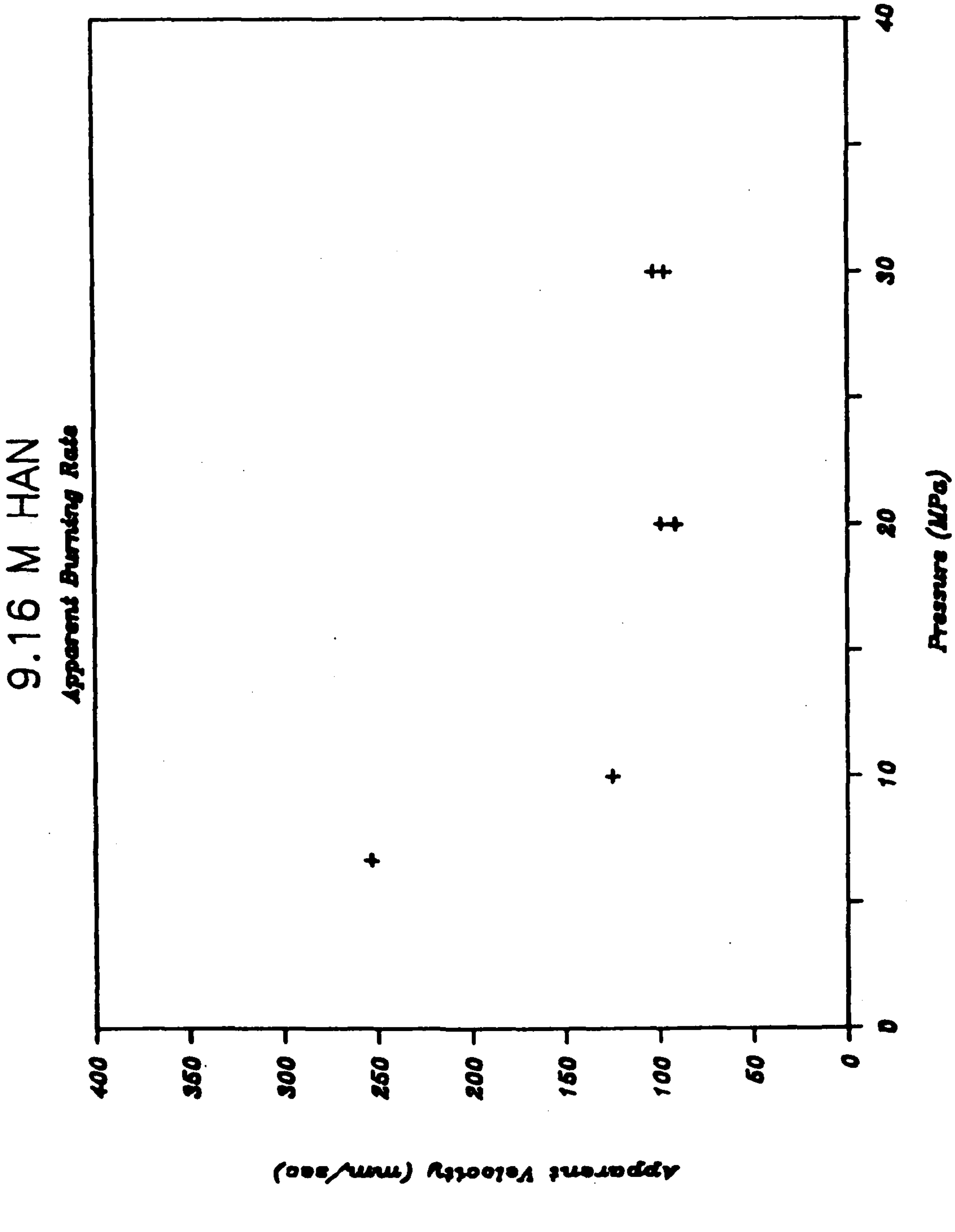
Effect of Spark Location

- Ignition below surface:
  - Visible flame stands off from liquid surface
  - No liquid is ejected from flame
  - Large pressure rise

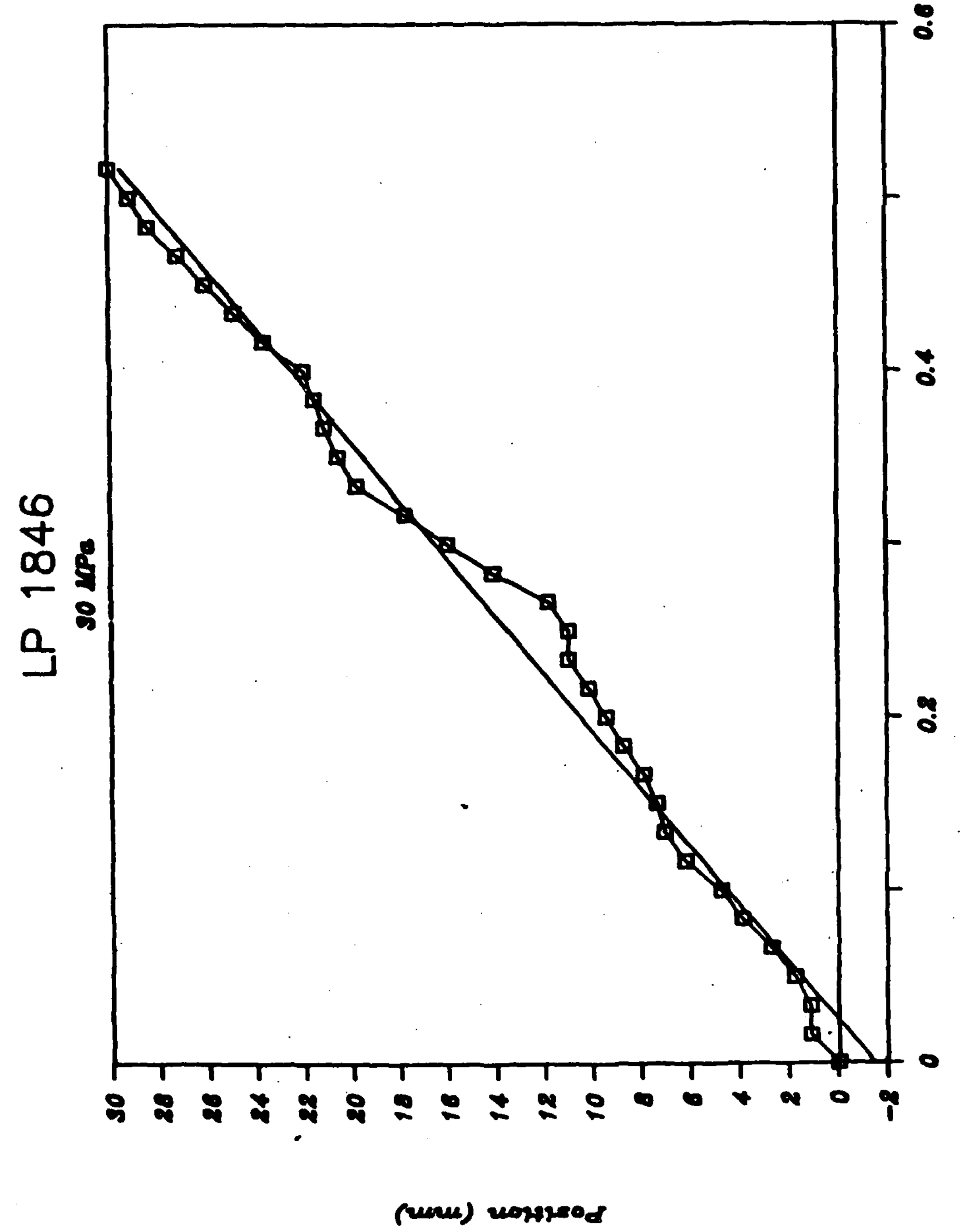
- Ignition at surface:
  - No visible flame is present
  - TEAN is ejected from the burner
  - Small pressure rise

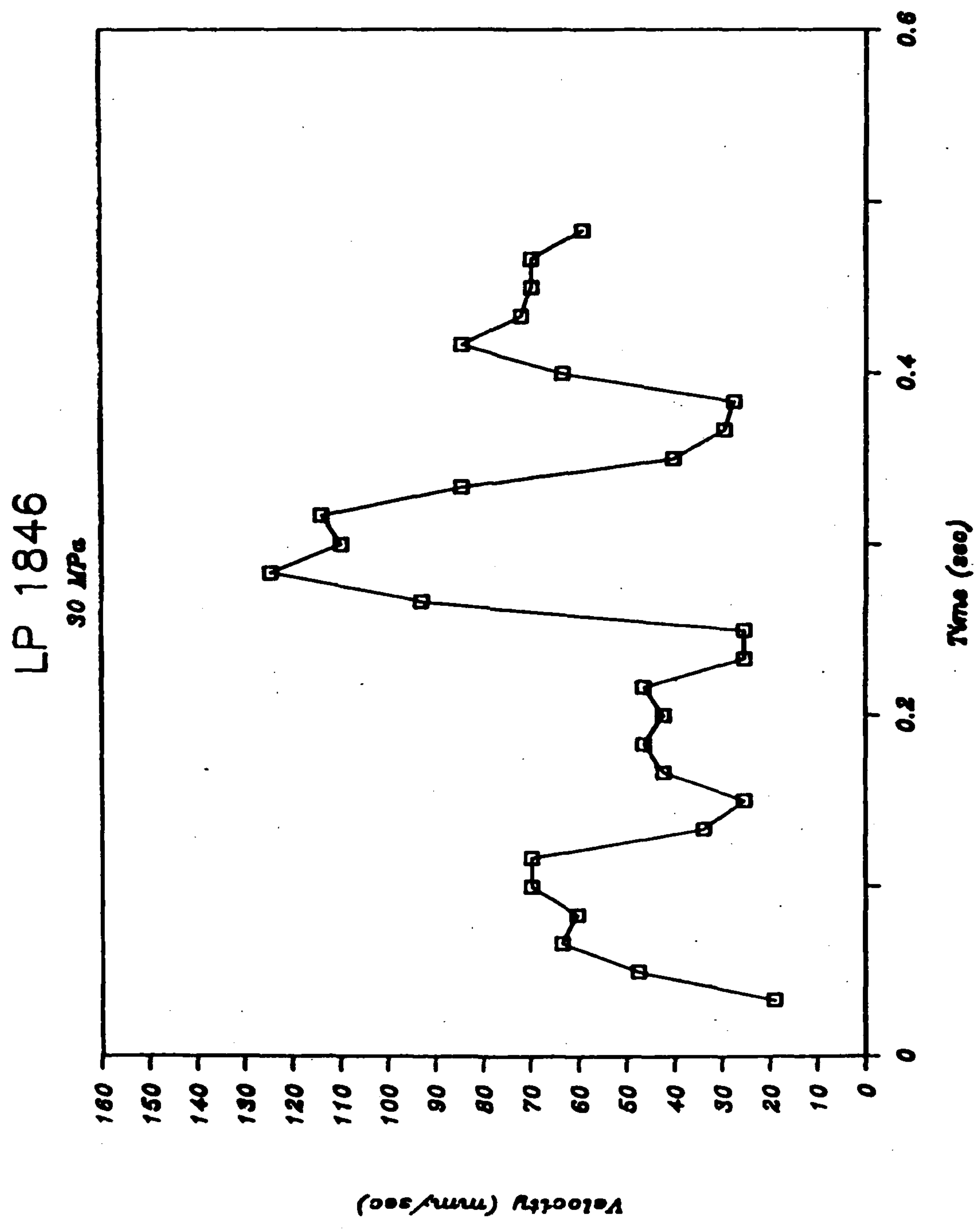
Model of HAN-TEAN-H_2O Combustion

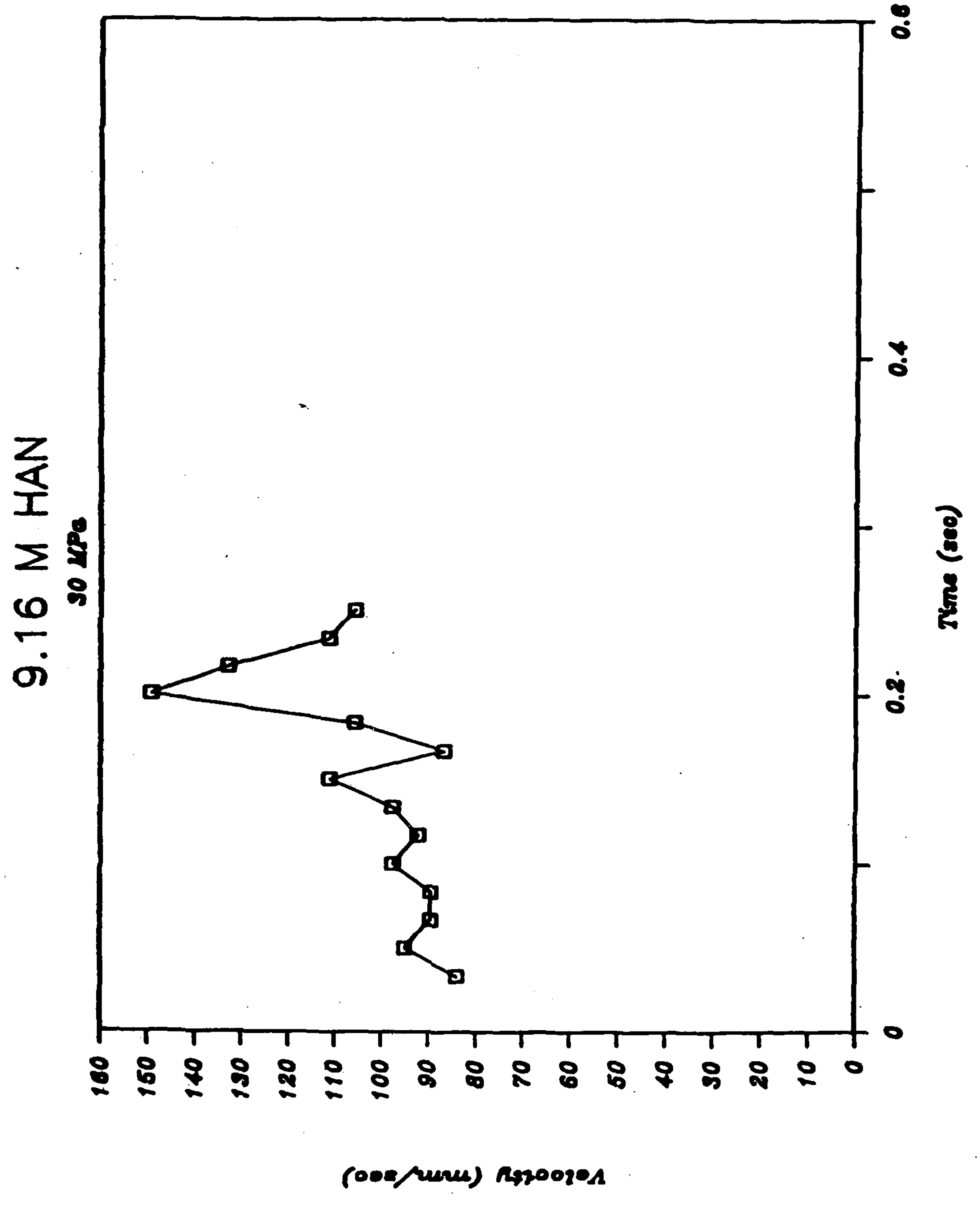




9.16 M HAN
Apparent Burning Rate
Apparent Velocity (mm/sec)
Pressure (MPa)
0
50
100
150
200
250
300
350
400
0
10
20
30
40


LP 1846
30 MPa
Position (mm)
Time (sec)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
0
0.2
0.4
0.6


LP 1846
30 MPa
Velocity (mm/sec)
Time (sec)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
0
0.2
0.4
0.6


9.16 M HAN
30 MPa
Velocity (mm/sec)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
Time (sec)
0
0.2
0.4
0.6

CONCLUSIONS

- HAVE VERIFIED THAT THE OVERALL REGRESSION RATE OF L.P. decreases with PRESSURE
- HAN decomposition also proceeds at a rate which decreases with pressure
- OSCILLATIONS occur which make it difficult to determine a laminar burning Speed

Requirements for Sequestering Agent

1) In low concentration, <1% by weight, must be able to strongly complex metal ions in presence of ten molar HAN

2) Must overcome nominal pH 4 in HAN

3) Complexed metal ions must be unreactive towards HAN

4) Must be chemically inert in harsh HAN environment (for years?)

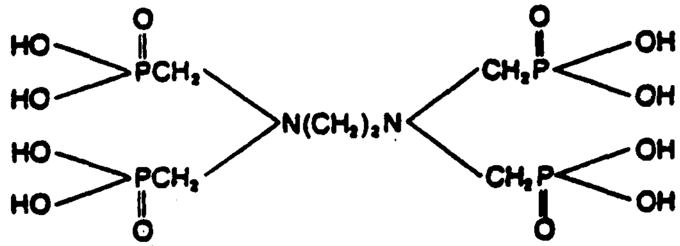
Stoichiometric Metal Ion Impurities

$$Cu(II) + HAN \rightarrow Cu(I) + N_2O + N_2 + (NO)$$

Catalytic Metal Ion Impurities

$$HAN \xrightarrow{Fe(III)} N_2O + (N_2)$$

Dequest 2041 (Monsanto)



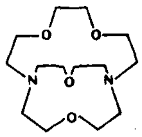
1) White solid, 94% purity (Monsanto)

2) White solid, 97% purity (Monsanto)

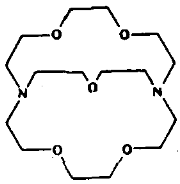
3) White solid, >99% purity (Dow)

4) Fully deprotonated form L^{8-} (ten protonation sites)

Kryptofix 211



Kryptofix 221



Donor atoms (O and N) enclosed in macrocyclic ring system.

Cryptate stability usually determined largely by match of ionic radius of metal ion and cavity radius of cryptand.

General Observations of Dequest Agents and Iron(III)

1) Fe(III) is promptly and extensively precipitated by 2041 and 2060 in both 2.8 M HAN and water ($pH < 6$), even at 0.5 mM Fe(III) and Dequest agent.

2) Solids obtained from either medium are very similar with a given Dequest agent. Fe(III)/Dequest ratio ca. 1:1 for 2041 and 3:2 for 2060.

3) Supernatants slowly deposit additional solid. Supernatants appear to be largely colloidal, but clearly contain complexed Fe(III).

4) Other metal ions [Cu(II), Co(II), Ni(II), Zn(II), Mn(II)] do not form precipitates, but are strongly complexed.

5) Iron(II) does not immediately form a precipitate, but later forms a white solid similar to that with iron(III).

6) The iron(III)-Dequest solids dissolve above pH 5-7 to form a yellow solution.

FIGURE ONE

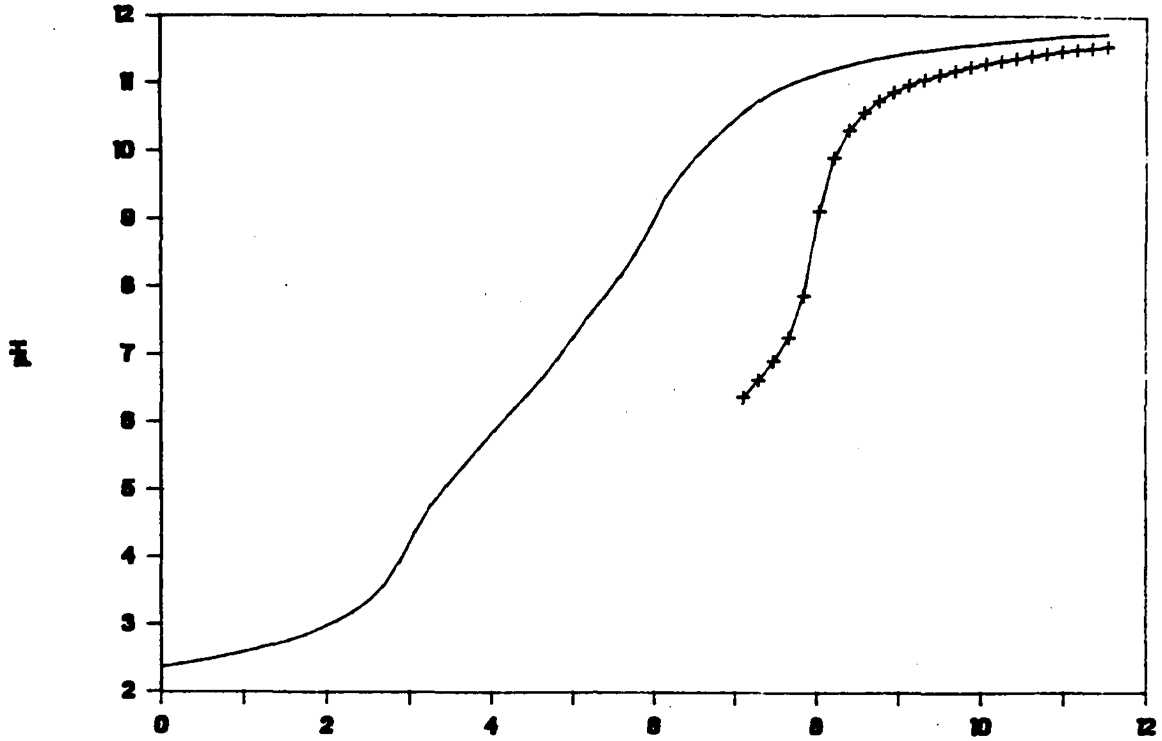
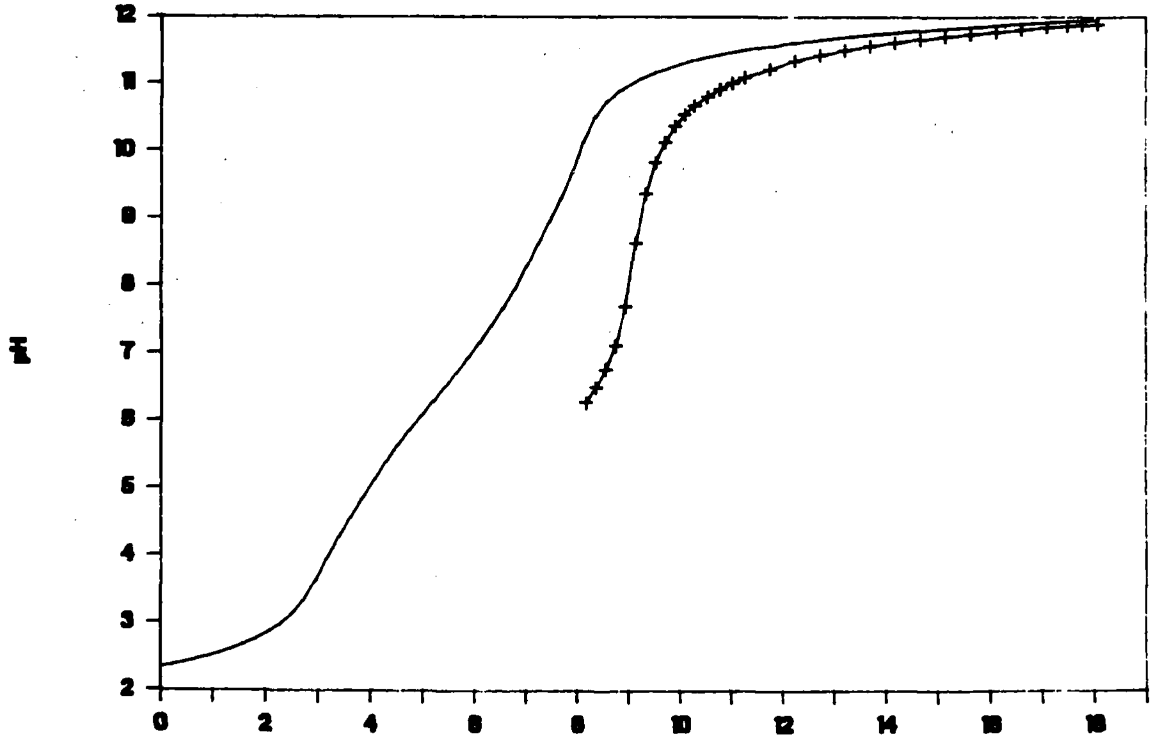


FIGURE TWO



2041

$$Fe(III) + L^{8-} \rightleftarrows FeL^{5-} \qquad \log K = 25.35$$

2060

$$Fe(III) + L^{10-} \rightleftarrows FeL^{7-} \qquad \log K = 24.24$$

Making the HAN–ELECTROCHEMICAL CONNECTION

Ronald L. Dotson

and

James A. Leistra

Olin Corporation

ABSTRACT

Hydroxylammonium nitrate, HAN, in high purity is a valuable chemical which can be produced by several different methods. It is active both as oxidizing and reducing agent, thereby making the electrochemical connection with its preparation and applications. The electrochemical synthesis of HAN has been the subject of considerable interest within recent years within Olin, and a process for its production being developed.

This talk provides a descriptive introduction to the fundamental properties of HAN and then moves quickly to the Olin approach to electrochemical synthesis from the viewpoint of electrochemical engineering. From this perspective the discussion emphasizes some of the unique design tools which the electrochemical engineer uses from both materials science and process design standpoints, that are not common to classical chemical engineering, such as current distribution, fluid flow patterns, mass and charge transfer under electrical load. Electrochemical engineering unifies the concepts of electrode reactions that are approached as heterogeneous catalysts, where the rates of the electrode reactions are controlled not only by the catalytic properties of the electrode substrate but also by the interplay of mass transfer mechanisms that determine the diffusion rate of electroactive species at the conductive and electroactive interfaces.

The discussion emphasizes the importance of correct choice of electrodes as well as materials and apparatus, and is given in four segments following the Introduction, Thermodynamics, Electro-kinetics, Transport and Separation, and finally last but not least Reactor Design.

HAN-ELECTROCHEM-CONNECTION

*DESCRIPTIVE INTRODUCTION

*THERMODYNAMIC PROPERTIES

*ELECTROKINETICS

*MASS TRANSPORT/SEPARATION

*PARALLEL PLATE REACTOR

*CONCLUSIONS

THE REDOX PROPERTIES OF HYDROXYLAMMONIUM NITRATE

[NH3OH] {NO3}

PROVIDE THE HAN-ELECTROCHEMICAL CONNECTION

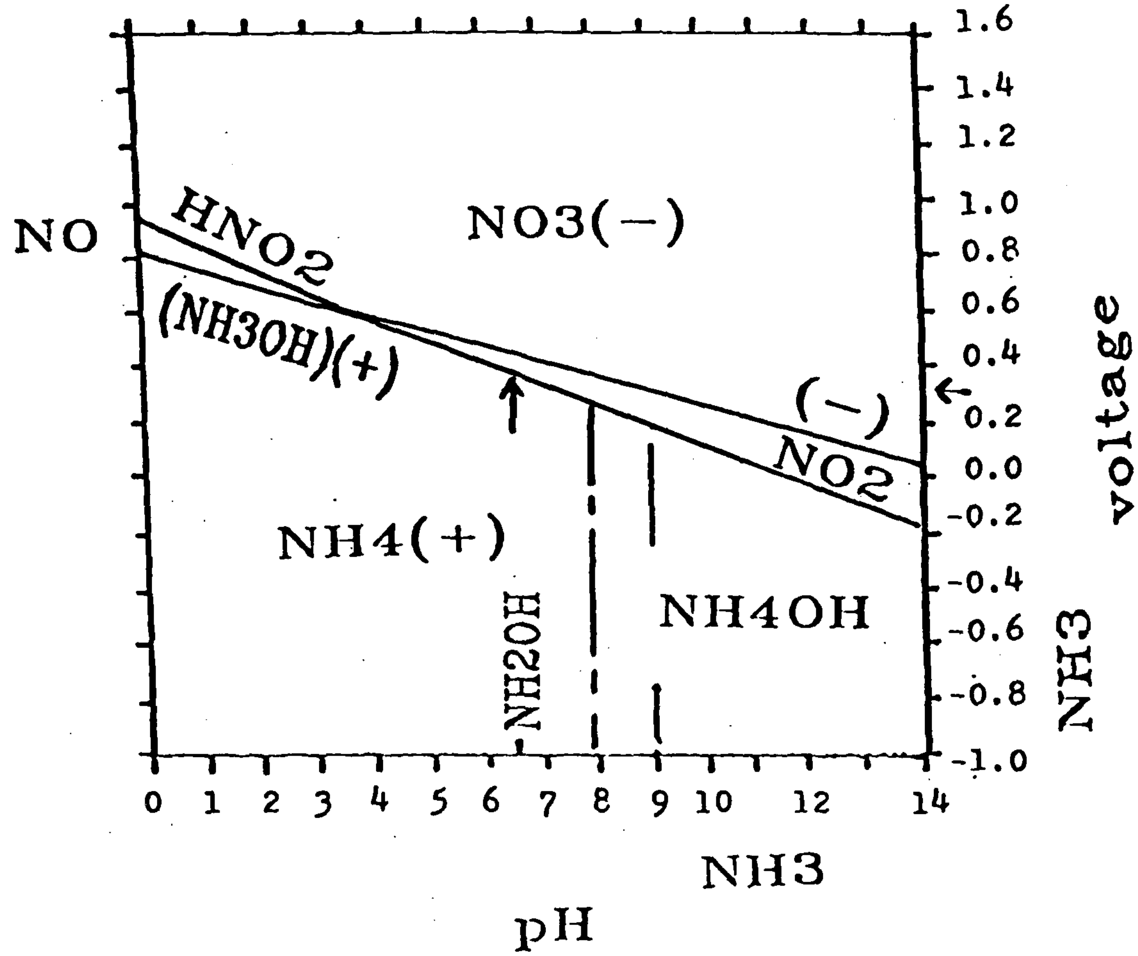
HYDROXYLAMMONIUM NITRATE IS DIFFERENT FROM THE OTHER HYDROXYLAMMONIUM SALTS

HAN can be formed by action of nascent hydrogen on Nitrogen Oxides:

```
HNO3 --> HNO2 --> NO ---> NH2OH ---> NH3
                      /---3e(-)-->/
   /-----------6e(-)---------->/

(+5)      (+3)     (+2)       (-1)       (-3)
<-------------Oxidation State------------->
```

POURBAIX DIAGRAM



THERMODYNAMICS

GIBBS RELATION

Relates the Gibbs free energy to cell voltage.

$$dG = -nFE$$

$$E(\text{volts}) = -4.184\ dG(\text{cals})/96{,}490n$$

GIBBS-HELMHOLTZ EQUATION

$$dG = dH - T[dS] = dH + T\{d(dG/dT)\}p$$

$$E = T(dE/dT)p - dH/nF$$

THERMODYNAMICS FOR NITRATE REDUCTION TO HAN

*CATHODE HALF CELL REACTION

$$6H(+) + 6e(-) + HNO_3 \longrightarrow NH_2OH + 2H_2O$$

*NERNST EQUATION

$$E = -0.720 + 0.069 \log [H(+)]$$

REACTION MECHANISM

*ELECTRODE KINETICS

CHARGE TRANSFER STEP:

H3O(+) + e(-) -----> H + H2O

PARAMETERS FOR ELECTRODE KINETICS

Tafel Equation:

$$\eta = (2.303RT/\alpha zF) \log [io/i]$$

$$H3O(+) + e(-) \text{ -----> } 0.5\ H2 + H2O$$

$$E = -2.303RT/F \log \{[H2]/[H(+)]\}$$

$$E = -1.984E-4\ (T)\ [pH]$$

MASS TRANSFER LIMITATIONS

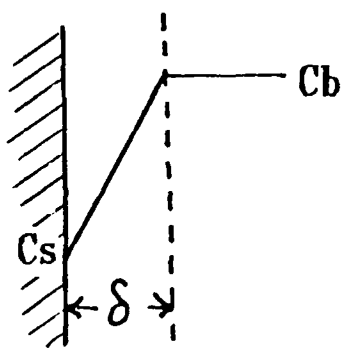
Concentration Polarization

Fick's Law

$$No = D/\delta\ (Cb - Cs)$$

Faraday's Law

$$i/zF = D/\delta\ (Cb - Cs)$$



Nernst Diffusion Layer

MASS TRANSFER LIMITATIONS

Concentration Overpotential

$$i(L)/zF = k\ Cb$$

$$Cb/Cs = i(L)/[i(L) - i]$$

$$\eta = a + b \log i + c \ln i(L)/[i(L) - i]$$

PROPOSED REDUCTION MECHANISM

Hydrodimerization of Nitro Groups by Indirect Coupling on Cathodic Mercury

$$2H + HNO_3 \longrightarrow H_3NO_3 \longrightarrow HNO_2 + H_2O$$

$$2H + HNO_2 \longrightarrow H_3NO_2 \longrightarrow HNO + H_2O$$

$$2HNO \longrightarrow \underline{H_2N_2O_2} \xrightarrow{2H} \underline{H_4N_2O_2} \xrightarrow{2H} \underline{H_6N_2O_2}$$

$$H_3NO{-}{-}NOH_3 \longrightarrow 2\ NH_2{-}OH$$

MASS TRANSFER IN ELECTROCHEMICAL SYSTEMS

1. $\vec{N}_i = -z_i u_i F c_i \vec{\nabla}\Phi - D_i \vec{\nabla} c_i + c_i \vec{v}$

2. $\partial c_i / \partial t = -\vec{\nabla} \cdot \vec{N}_i + R_i$

3. $\Sigma_i z_i c_i = 0$

4. $\vec{i} = F \Sigma_i z_i \vec{N}_i$

APPLICATION TO ELECTROLYTIC PRODUCTION OF HAN

For Binary Electrolyte

$$\partial c/\partial t + \vec{v} \cdot \vec{\nabla} c = z_+ u_+ F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + D_+ \nabla^2 c$$

$$\partial c/\partial t + \vec{v} \cdot \vec{\nabla} c = z_- u_- F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + D_- \nabla^2 c$$

Subtracting Yields

$$(z_+ u_+ - z_- u_-) F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + (D_+ - D_-) \nabla^2 c = 0$$

Substituting for the Potential Yields

$$\partial c/\partial t + \vec{v} \cdot \vec{\nabla} c = D \nabla^2 c$$

Where $D = (z_+ u_+ D_- - z_- u_- D_+)/(z_+ u_+ - z_- u_-)$

CURRENT DISTRIBUTION AT ELECTRODE SURFACE

Velocity (y-direction) = 0
Only the cation reacts at the cathode

Cation Flux

$$N_+ = i/z_+ F = -z_+ u_+ F\nu_+ c\,(\partial \Phi/\partial y) - D_+\nu_+ (\partial c/\partial y)$$

Anion Flux

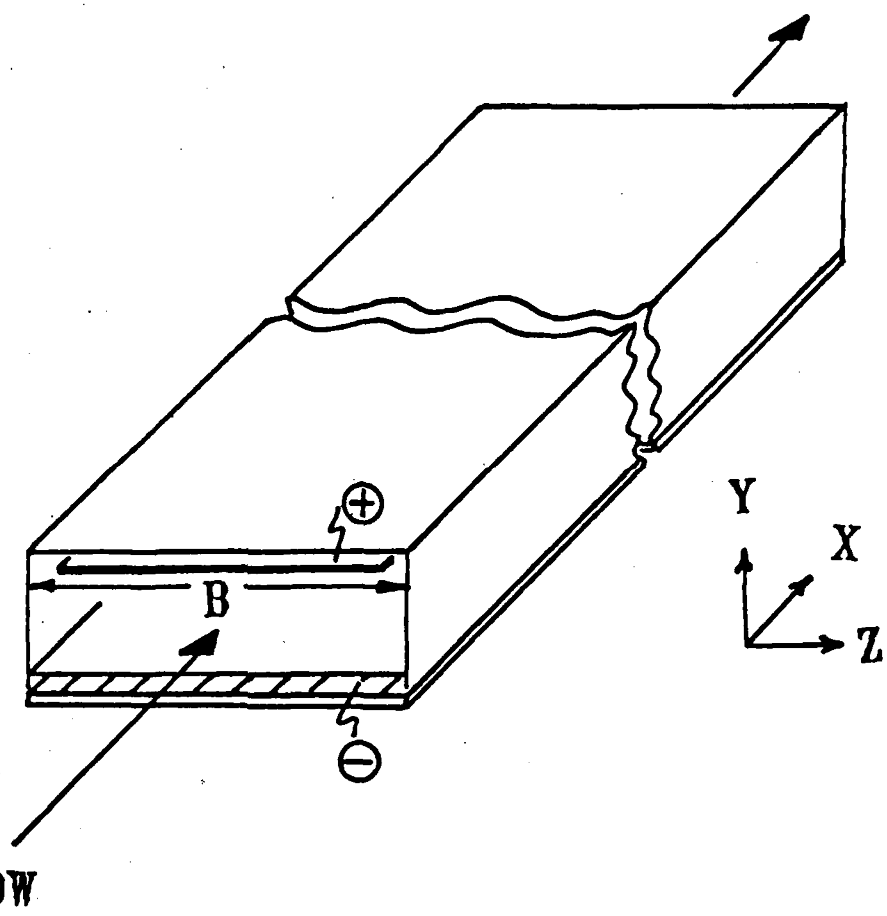
$$N_- = 0 = -z_- u_- F\nu_- c\,(\partial \Phi/\partial y) - D_-\nu_- (\partial c/\partial y)$$

Where $c = c_+/\nu_+ = c_-/\nu_-$

Eliminating the Potential Gradient

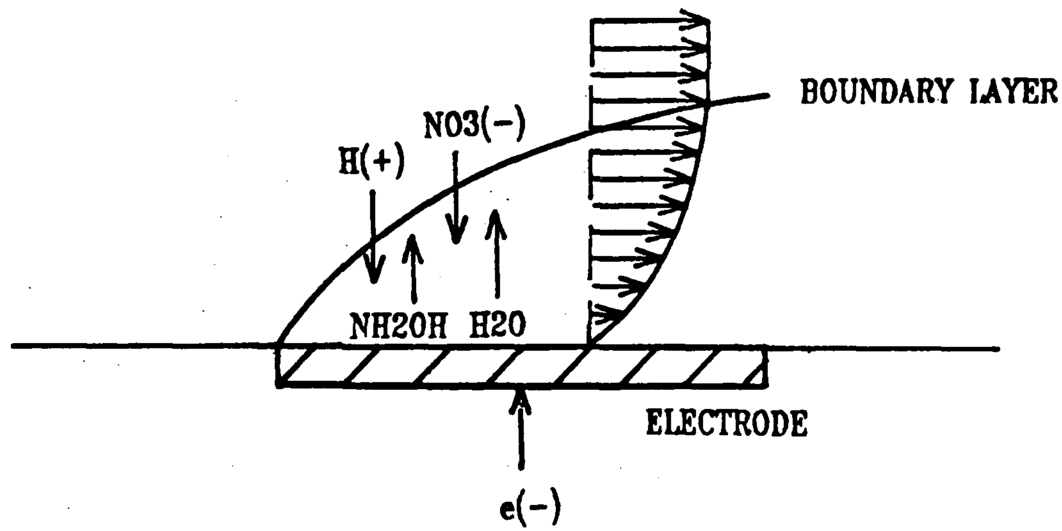
$$i/z_+\nu_+F = -[(z_- u_- D_+ - z_+ u_+ D_-)/ z_- u_-]\, \partial c/\partial y$$

PARALLEL PLATE REACTOR WITH ELECTRODES OF FINITE WIDTH



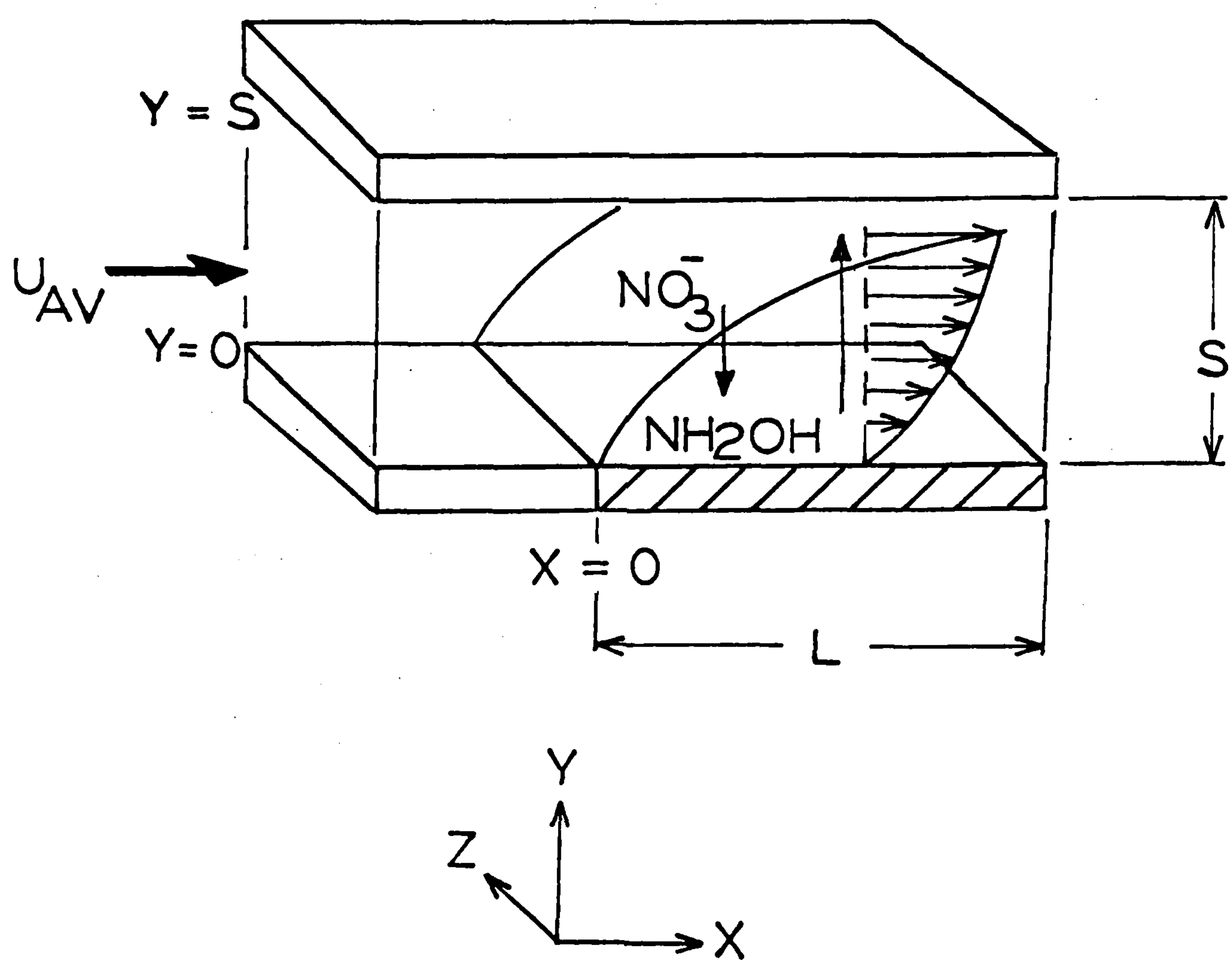
FLOW AND MASS TRANSFER IN THE HYDRODYNAMIC ENTRANCE REGION OF A PARALLEL PLATE ELECTROCHEMICAL REACTOR

$$7\,H^{+} + 6\,e^{-} + NO_3^{-} \longrightarrow NH_2OH + 2\,H_2O$$



PARALLEL PLATE REACTOR

Hydrodynamic entrance length under laminar, forced-flow conditions



PARALLEL PLATE REACTOR

Goal: $i_x = \text{fcn}(x)$

$$i_x = z F K_x (C_b - C_s)$$

where $K_x = [-D/(C_b - C_s)] (\partial C/\partial y)_{y=0}$

or $i_x = z F (C_b - C_s) Sh_l D/d_e$

where $Sh_l = K_x d_e/D$

PARALLEL PLATE REACTOR

General Differential Equation

$$\partial C_j/\partial t + \vec{u} \cdot \vec{\nabla} C_j = z_j u_j F \vec{\nabla} \cdot (c_j \vec{\nabla} \Phi) + D_j \nabla^2 C_j$$

For steady state operation
small potential gradient
2 - dimensional flow

$$u_x (\partial C/\partial x) + u_y (\partial C/\partial y) = D (\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2)$$

For fully developed laminar flow
negligible diffusion in x - direction

$$u_x (\partial C/\partial x) = D (\partial^2 C/\partial y^2)$$

PARALLEL PLATE REACTOR

Need an expression for $u_x = \text{fcn}(y)$

from Navier-Stokes equation

$$u_x = 6\, U_{av}\, [y/S - y^2/S^2]$$

from Leveque approximation

$$u_x = 6\, U_{av}\, y/S$$

Therefore:

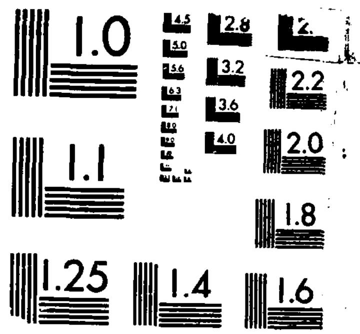
$$[6\, U_{av}\, y/S]\, \partial C/\partial x = D\, (\partial^2 C/\partial y^2)$$

with $C = C_s$ at $y = 0$ for $x>0$

$C = C_b$ at $x = 0$ for $0<y<S$

AD-A194 679 THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS 3/3
(3RD) HELD IN ABERD..(U) ARMY BALLISTIC RESEARCH LAB
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL. MAR 88

UNCLASSIFIED BRL-SP-73 F/G 19/1 NL



MICROCOPY RESOLUTION TEST CHART
URFAU OF STANDARDS-1963-A

PARALLEL PLATE REACTOR

Solution to the basic differential equation

$$K_x = (D/0.893)\,[2\,U_{av}/(3\,D \times S)]^{1/3}$$

$$Sh_l = 1.23\,[Re\,Sc\,d_e/x]^{1/3}$$

or for the whole reactor

$$Sh_{av} = 1.85\,[Re\,Sc\,d_e/L]^{1/3}$$

with

$$i = z\,F\,(C_b - C_s)\,Sh\,D/d_e$$

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

EMULSIFIED HAN-BASED PROPELLANTS

BY

NEALE A. MESSINA

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

A PRESENTATION AT

U.S. ARMY BALLISTIC RESEARCH LABORATORY

CONFERENCE ON HAN-BASED LIQUID PROPELLANT

STRUCTURE AND PROPERTIES

26 AUGUST 1987

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

ACKNOWLEDGEMENT

- PHASE I SMALL BUSINESS INNOVATIVE RESEARCH (SBIR) PROGRAM
- U.S. ARMY ARDEC CONTRACT DAAA21-86-C-0232
- COTR: DR. ARTHUR BRACUTI

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

PROGRAM PLAN

- FORMULATION: IDENTIFICATION OF CANDIDATE FUELS
- THERMOCHEMICAL EQUILIBRIUM PERFORMANCE (LPG 1845 BASELINE; IMPETUS = 980 j/g, $T_f = 2723$ K)
- PROCESSING OF 13M HAN/FUEL/EMULSIFYING AGENT
  - FORMULATION WITH THEORETICAL IMPETUS $\geq$ 980 j/g
  - PERMANENCE OF EMULSION
  - OXIDIZER DROPLET SIZE

PROGRAM PLAN (CONT'D)

- RHEOLOGICAL PROPERTIES
  - SHEAR STRESS VERSUS SHEAR RATE; THIXOTROPY
  - YIELD POINT BEHAVIOR
  - DYNAMIC LOADING THROUGH GUN VALVE
- IMPACT SENSITIVITY
- THERMAL INITIATION CHARACTERISTICS

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

WHY COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs?

- OPERATIONAL SHORTCOMINGS OF BULK-LOADED LIQUID MONOPROPELLANT GUNS
  - INCONSISTENT BALLISTIC PERFORMANCE, UNPREDICTABLE IGNITION, OCCASIONAL HIGH PRESSURE PEAKS
  - BALLISTICS ARISE OUT OF INTERACTION BETWEEN HYDRODYNAMIC INSTABILITIES AND COMBUSTION OF HIGHLY VARIABLE SURFACE AREA OF MONOPROPELLANT CHARGE; TAILORING IS A PROBLEM
  - SENSITIZATION OF BULK MONOPROPELLANT CHARGE; COMPRESSION IGNITION SENSITIVITY ASSOCIATED WITH ENTRAPPED BUBBLES AND ULLAGE

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

WHY COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs ?(CONT'D)

- OPERATIONAL SHORTCOMINGS OF REGENERATIVE LIQUID MONOPROPELLANT GUNS

  - SENSITIVITY/HAZARDS OF LIQUID MONOPROPELLANT; COMPRESSION IGNITION, FRICTIONAL SENSITIVITY OF HIGH SPEED FLOW IN NARROW GAPS

  - LOW PRESSURE COMBUSTION INADEQUACIES

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

WHAT DO COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs OFFER?

- WELL-DEFINED SURFACE AREA OF OXIDIZER DROPLETS EXISTS AS SITES FOR COMBUSTION REACTIONS
- GAS GENERATION RATE LESS SENSITIVE TO SURFACE AREA GENERATION DUE TO HYDRODYNAMIC BREAK-UP AND INSTABILITIES
- RATE OF REACTION "DESIGNED" INTO PROPELLANT BY SUITABLE CHOICE OF OXIDIZER DROPLET SIZE, IMMISCIBLE FUEL COMPONENT, STOICHIOMETRY

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

WHAT DO COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs OFFER? (CONT'D)

- OBVIATE NEED FOR MISCIBILITY AS REQUIRED FOR SOLUTION MONOPROPELLANTS
- POTENTIAL REDUCED SENSITIVITY DUE TO HETEROGENEITY (INTERDIFFUSION PROCESS AT INTERFACES)
- GROWTH POTENTIAL TO HIGH ENERGY FORMULATIONS FOR 120mm TANK GUN

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

COMPOSITE EMULSIFIED PROPELLANT CONSTITUENTS, "WATER-IN-OIL" EMULSIONS

- CONCENTRATED AQUEOUS SOLUTION OF 13M HAN, DISPERSED PHASE OXIDIZER
- HYDROCARBON FUEL IMMISCIBLE IN WATER
  - ALIPHATIC HYDROCARBONS (n-DECANE, ISO-OCTANE)
  - AROMATIC HYDROCARBONS (TOLUENE)
  - HIGH ENERGY NITROPLASTICIZERS (BDNPA-F, n-butylNENA)
- EMULSIFYING AGENT (HYDROPHILE/LIPOPHILE BALANCE)
  - FATTY ACIDS
  - FATTY ACID ESTERS
- WIDE RANGE OF PERFORMANCE VALUES ATTAINABLE
- DROPLET SIZE ADJUSTABLE

  $<$ 1 MICRON (MICROEMULSION)

  10-100 MICRON (MACROEMULSION)

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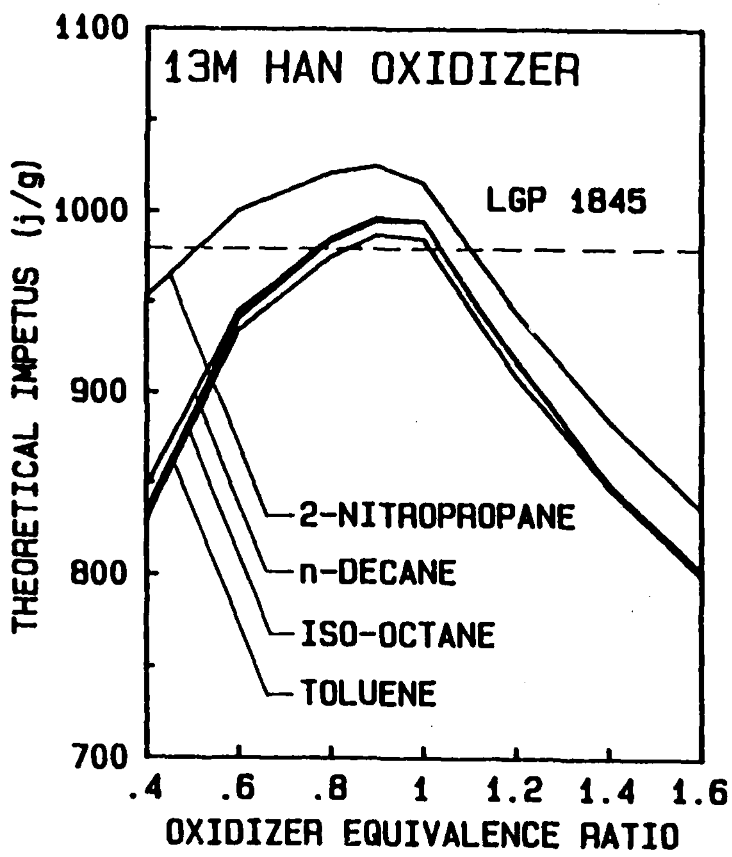
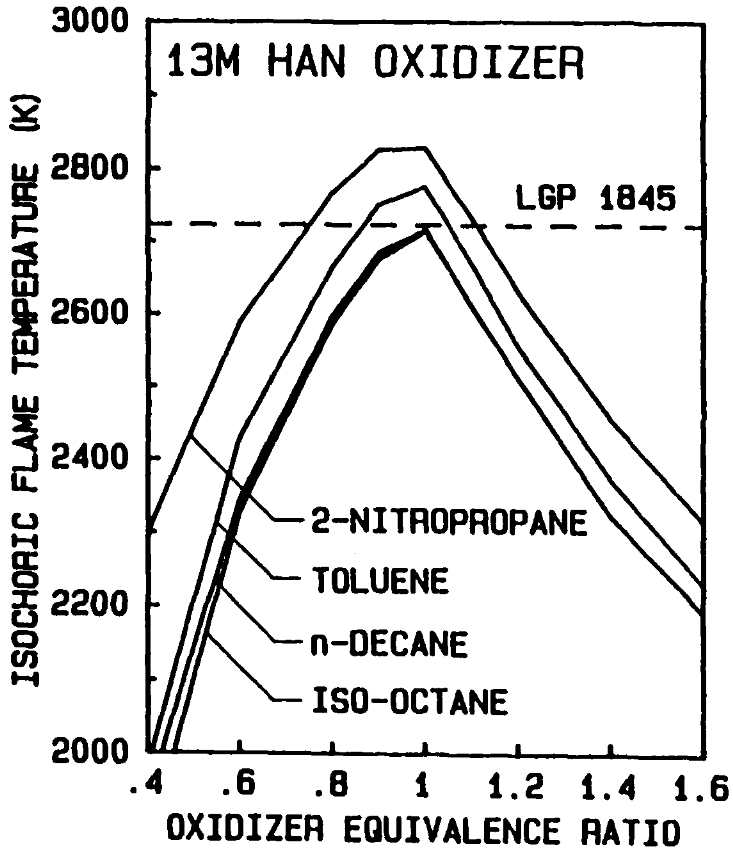
EQUILIBRIUM THERMOCHEMISTRY





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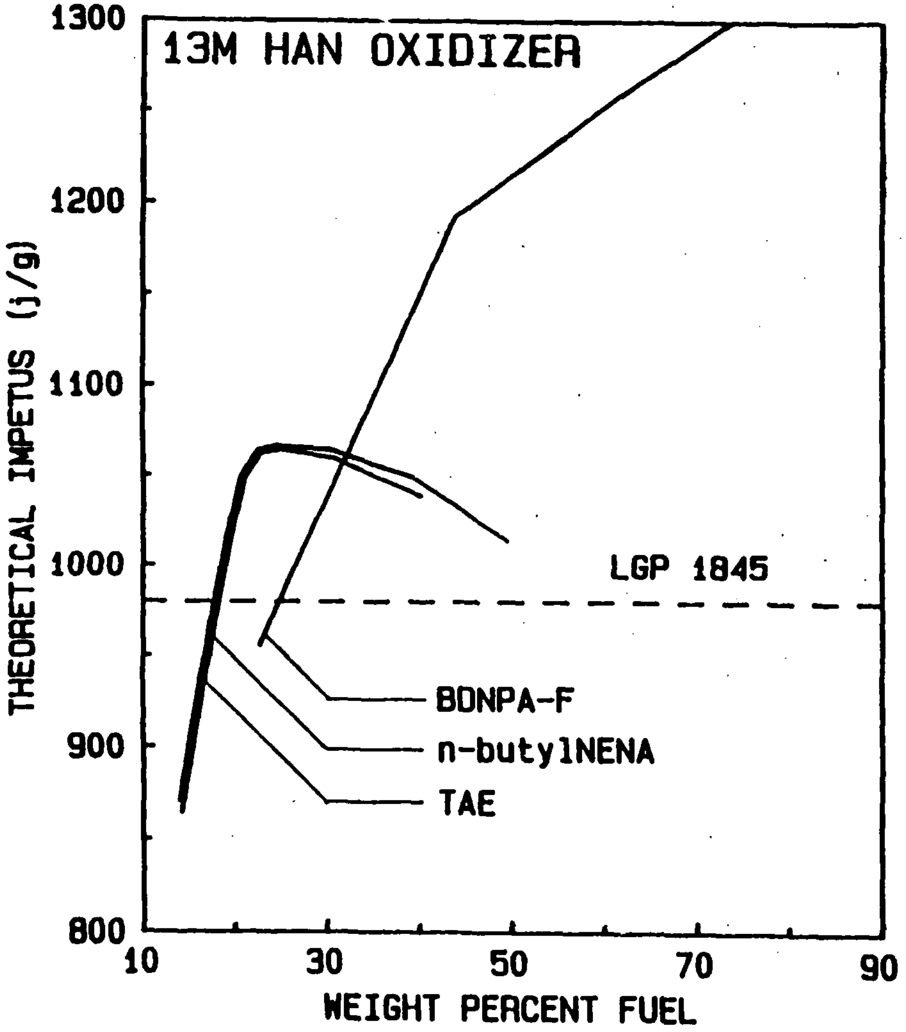
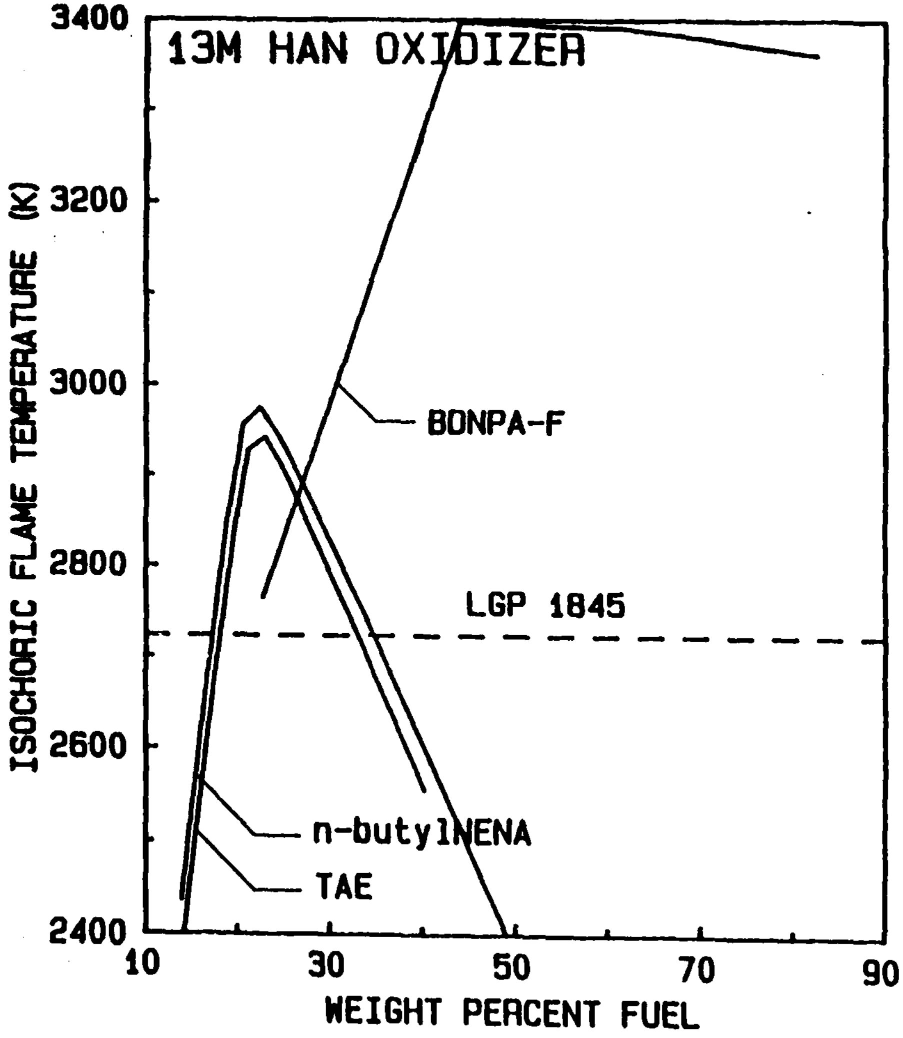
EQUILIBRIUM THERMOCHEMISTRY





PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

EMULSIFICATION TECHNIQUES

- SONIFICATION (HIGH FREQUENCY VIBRATION)
- MICROFLUIDIZATION (IMPINGING STREAMS)
- MECHANICAL MIXERS, TUMBLERS
- ROTOR-IN-STATOR HOMOGENIZERS

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

PROPELLANT PROCESSING

CONSTITUENT WEIGHT PERCENT			MEAN DROPLET SIZE	MAX DROPLET SIZE	PERMANENCE	CONSISTENCY[†]
HAN	H_2O	FUEL	(MICRON)	(MICRON)	(DAYS)	
74.8	17.3	7.9 n-DECANE	0.5-1	3	>30	10
74.8	17.3	7.9 n-DECANE	1-10	50	>30	5
74.8	17.3	7.9 ISO-OCTANE	1-5	100	21	8
74.1	17.1	8.8 TOLUENE	1-15	250	>7	7
24.3	5.6	70.1 BDNPA-F	1-5	5	21	5
49.3	11.4	39.3 n-butylNENA	--	--	NOTE 1	10

[†] 10 ≡ PASTE-LIKE
1 ≡ WATER-LIKE

NOTE 1. FUME-OFF OBSERVED WITHIN 8 HR TO THREE DAYS OF STORAGE

PHOTOMICROGRAPHS

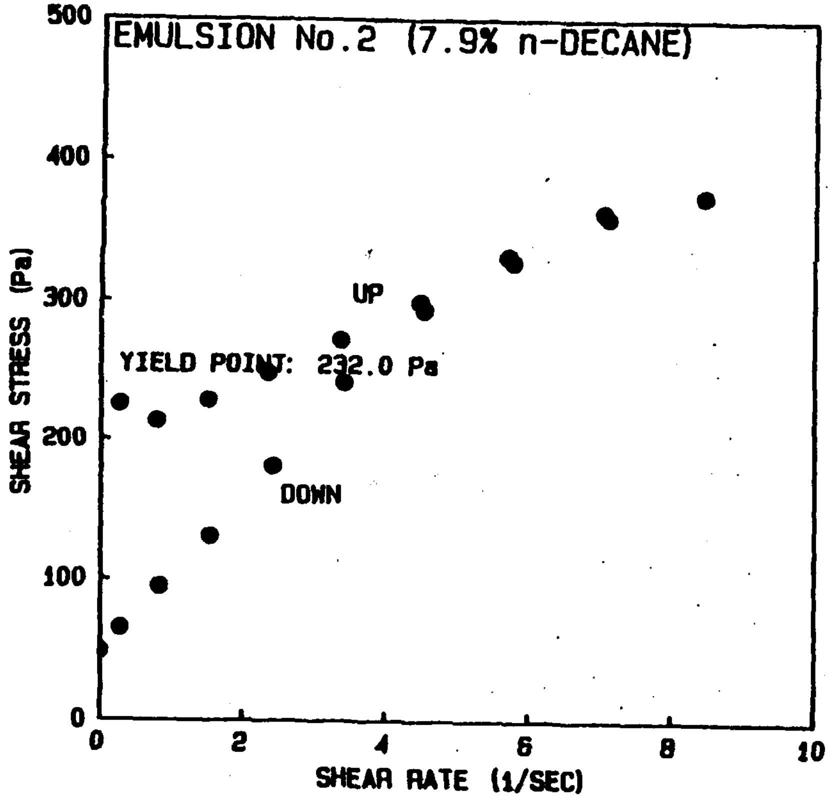
OF EMULSIFIED HAN-BASED LIQUID PROPELLANTS

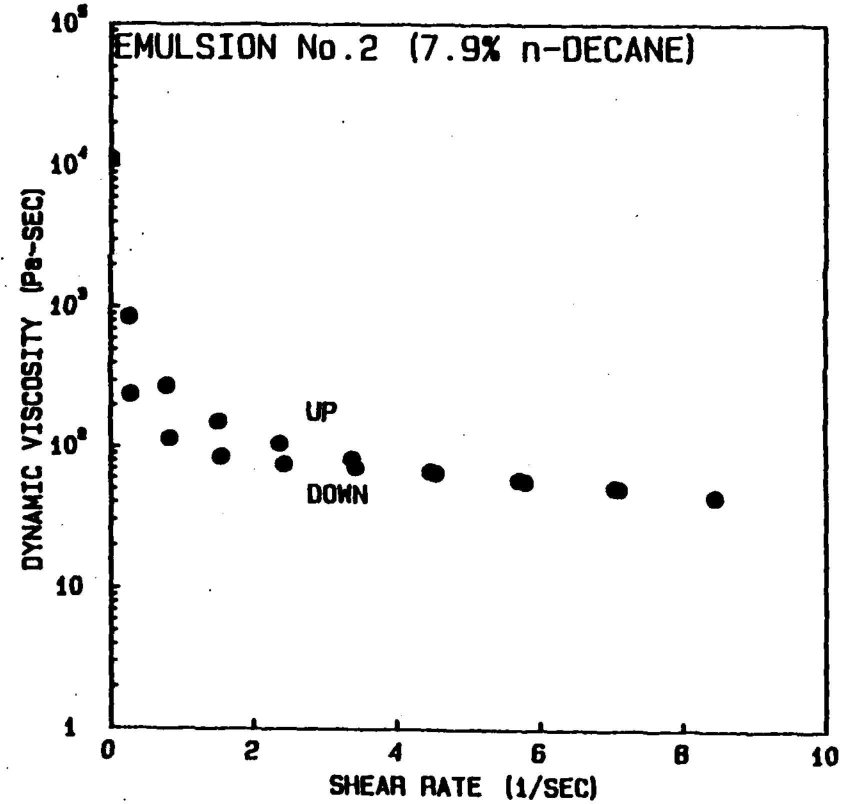
PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

RHEOLOGICAL PROPERTIES

- NON-NEWTONIAN LIQUIDS
- THIXOTROPIC, TO VARYING DEGREES
- YIELD POINT EXHIBITED, 2.3 Pa - 232 Pa

RHEOLOGICAL PROPERTIES





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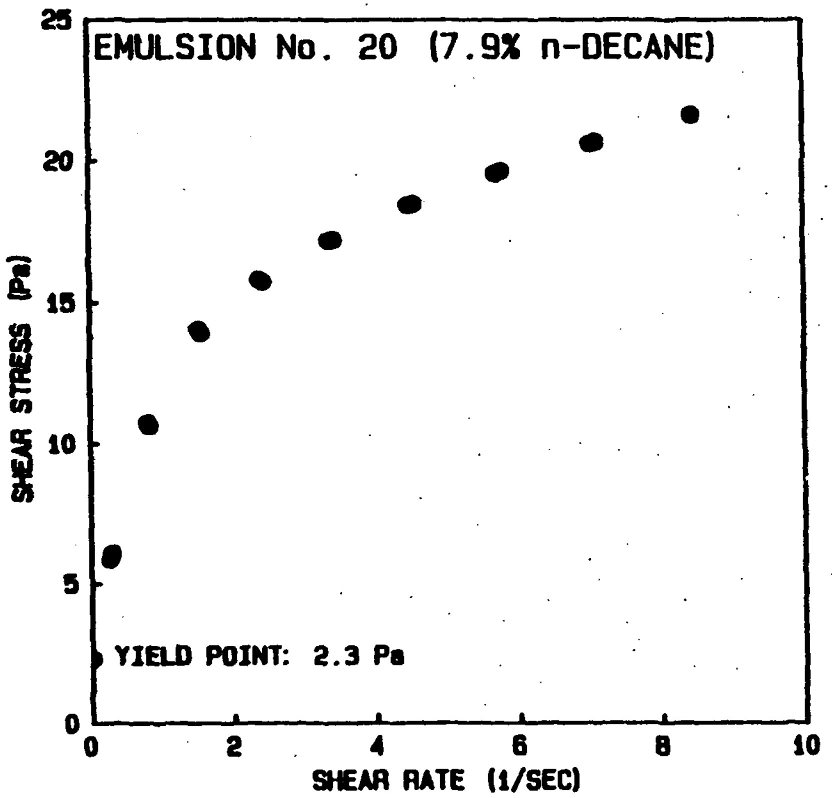
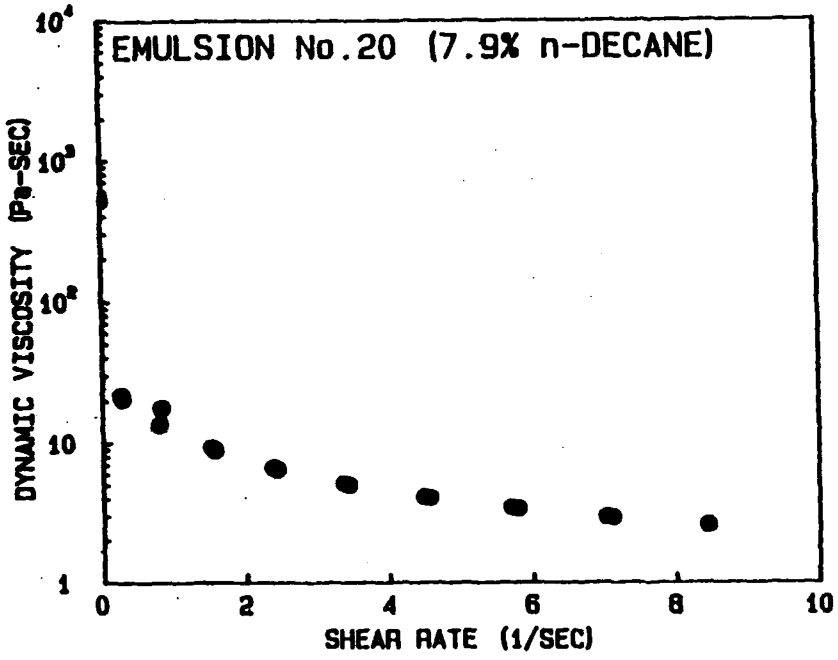
RHEOLOGICAL PROPERTIES





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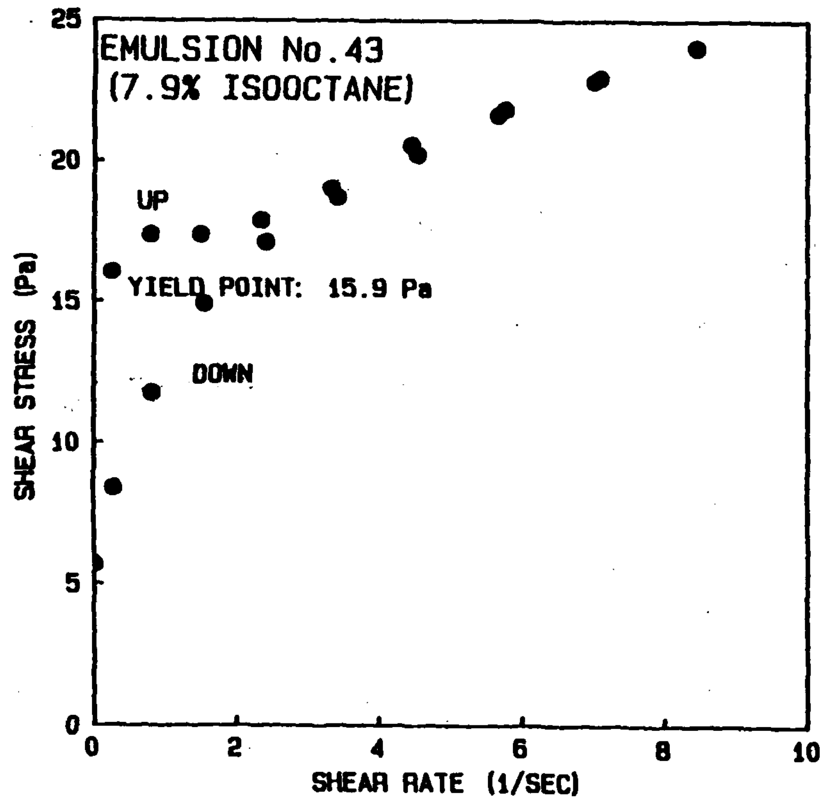
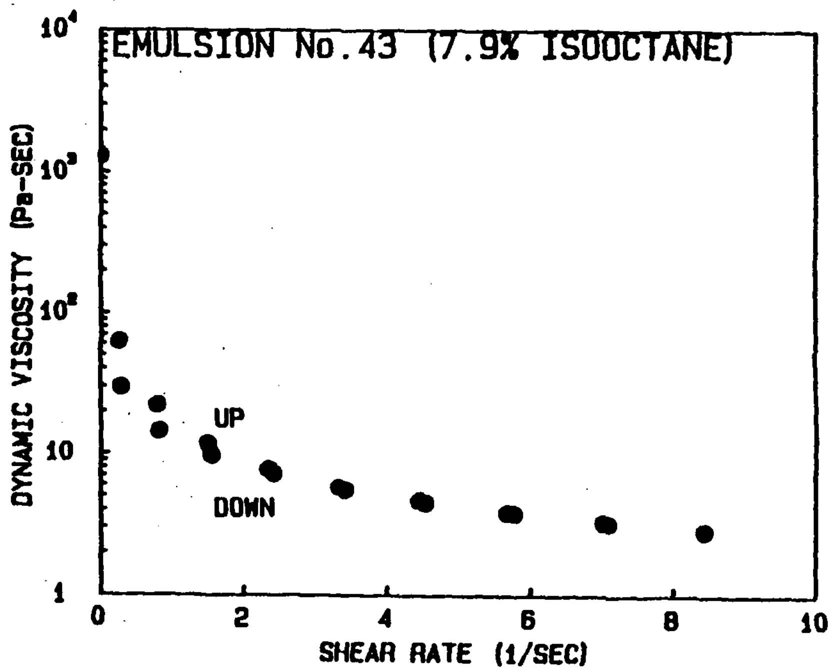
RHEOLOGICAL PROPERTIES





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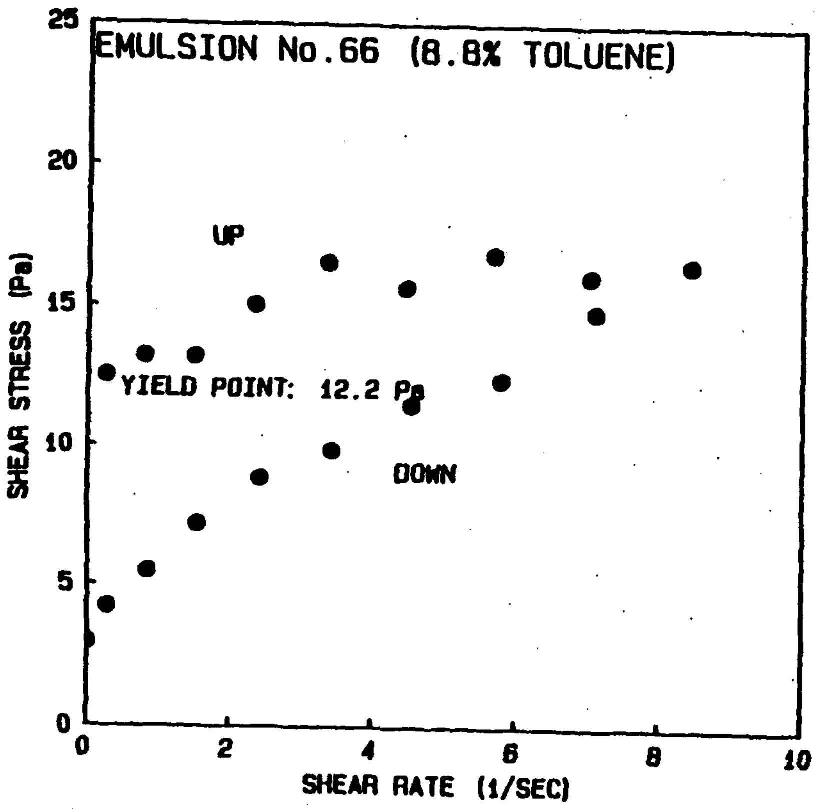
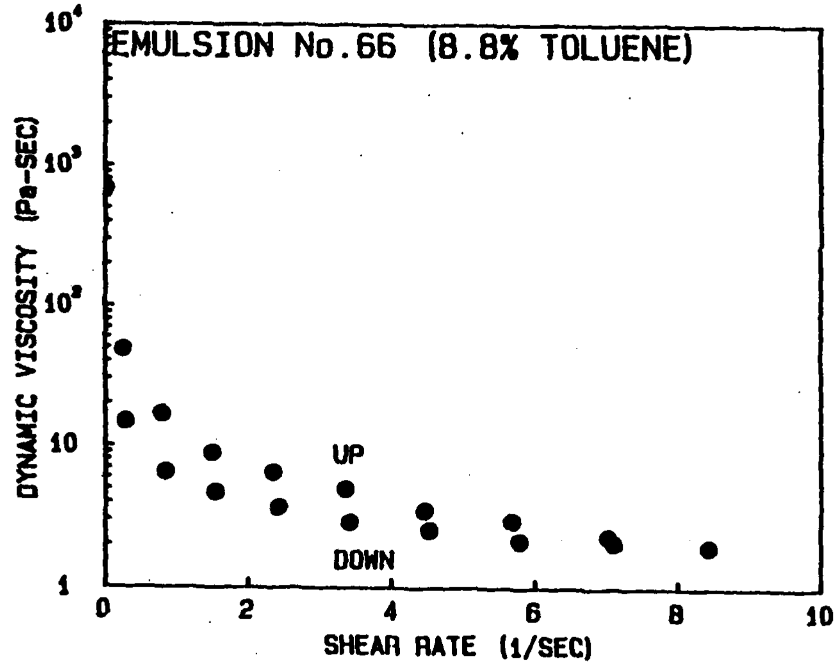
RHEOLOGICAL PROPERTIES





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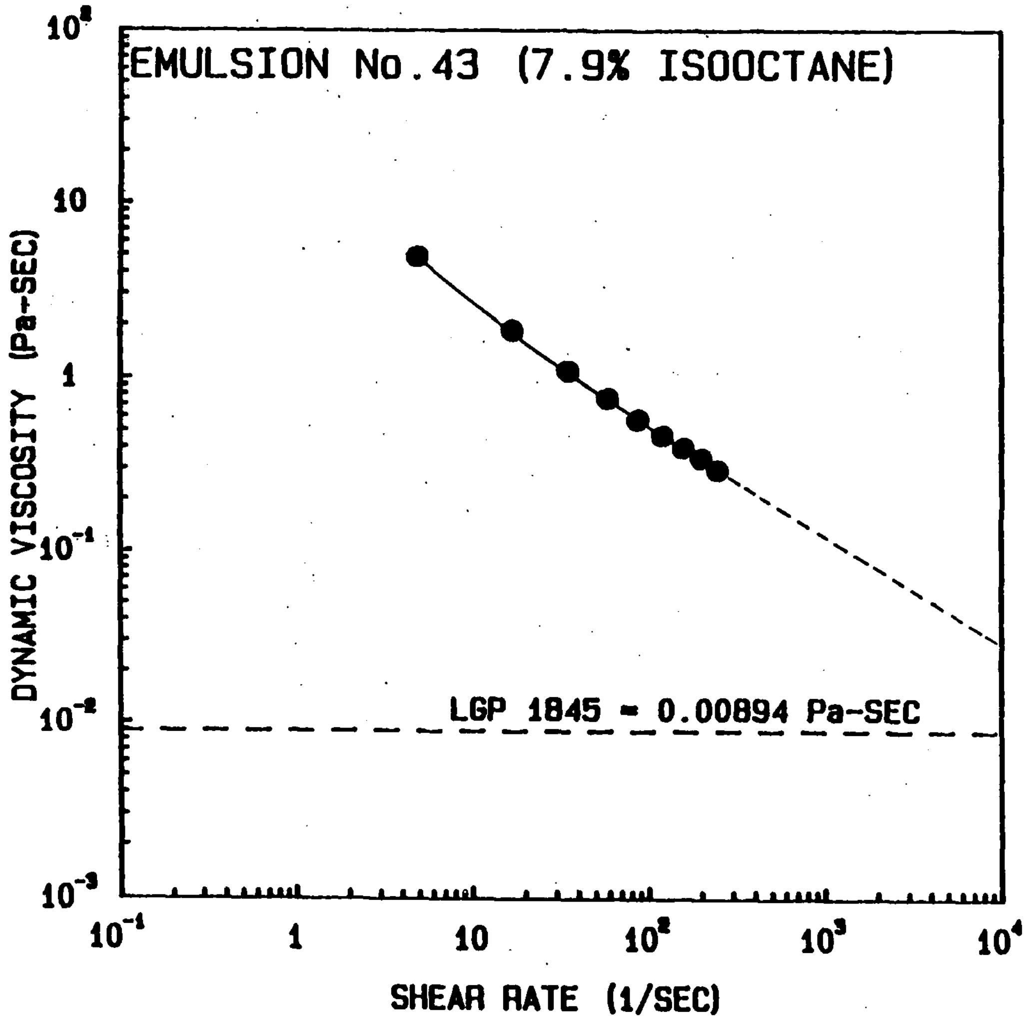
HIGH SHEAR RATE BEHAVIOR



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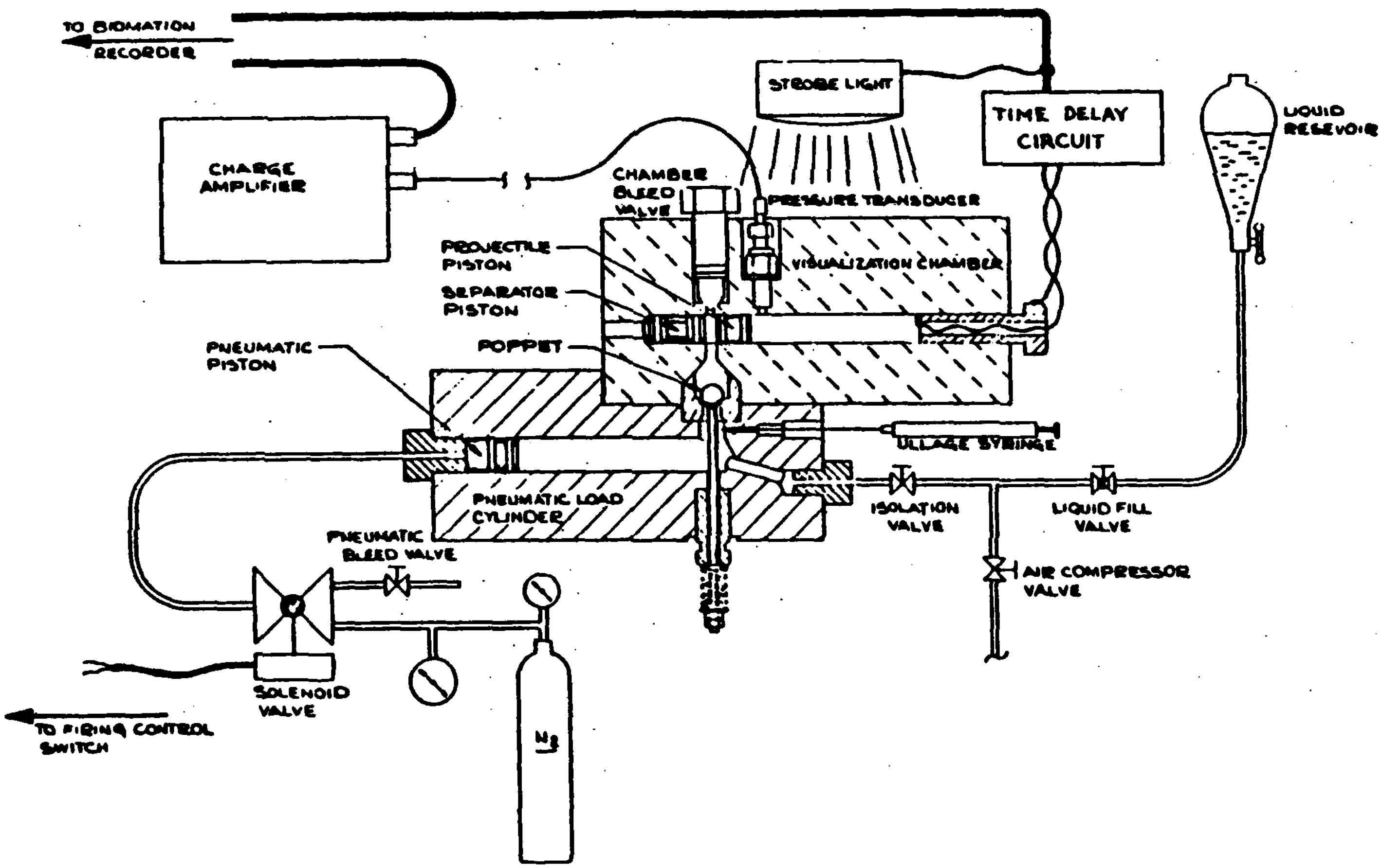
DYNAMIC LOADING BEHAVIOR THROUGH GUN VALVE



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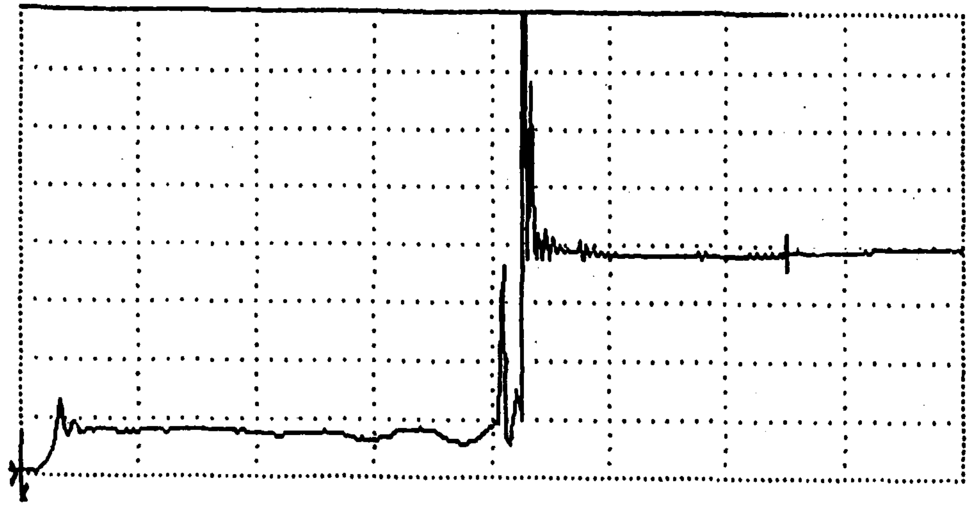
DYNAMIC LOADING
EMULSION NO. 20(n-DECANE)



SCALING

PRESSURE: 100PSI/DIV

TIME: 5 msec/DIV

t_{INJECT} =21.2msec

P_{EQUIL} =382PSIG

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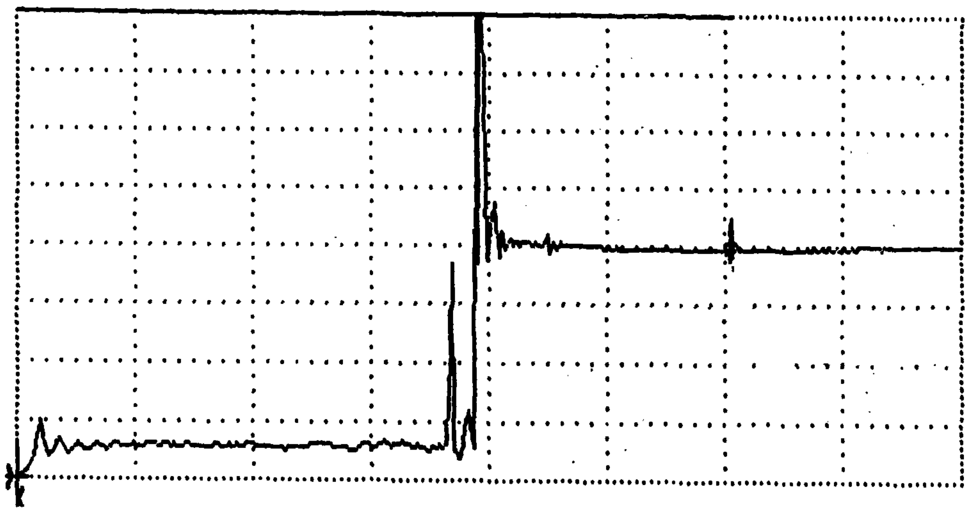
DYNAMIC LOADING
LGP 1845



SCALING

PRESSURE: 100PSI/DIV

TIME: 5msec/DIV

t_{INJECT} =19.3 msec

P_{EQUIL} =400PSIG

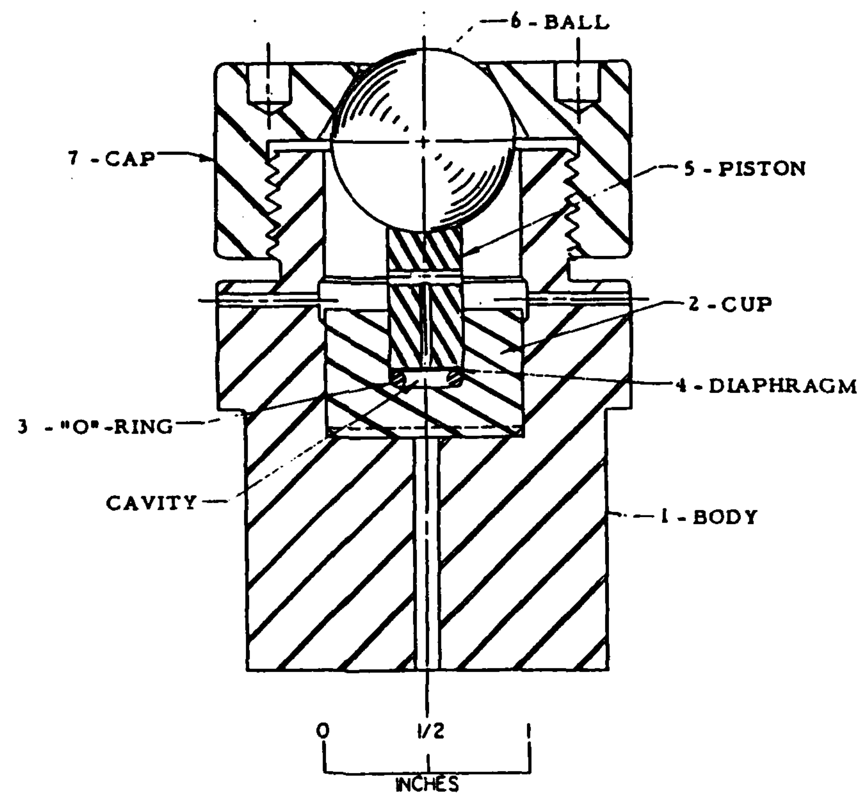
PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

IMPACT SENSITIVITY

TECHNOPRODUCTS DROP WEIGHT TESTER; 4 kg WEIGHT

HYDRAULIC LIMIT (85%) = 157.9 kg-cm

SAMPLE HOLDER



PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

IMPACT SENSITIVITY FOR SOLUTION MONOPROPELLANTS

50% IGNITION POINT (kg-cm)

PROPELLANT	PREVIOUS TESTS	CURRENT STUDY
Otto Fuel II	8.5 - 70 [4] 98 [1]	102.0
NOS-365	>100 [3] 98 [1] 152 [2]	140.8
LGP 1845	>100 [1] 152 [2]	154.6

REF. 1 STOBIE, U.S. ARMY BRL
2 CRUICE, HAZARDS RESEARCH
3 SMITH, NSWC
4 MASON, BUREAU OF MINES

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

IMPACT SENSITIVITY FOR HETEROGENEOUS EMULSIONS

PROPELLANT		50% IGNITION POINT (kg-cm)
EMULSION NO. 20	(n-DECANE)	156.0
EMULSION NO. 43	(ISO-OCTANE)	155.0
EMULSION NO. 66	(TOLUENE)	>158.0
EMULSION NO. 38	(BDNPA-F)	20.0

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

CONCLUSIONS

- STABLE "WATER-IN-OIL" HETEROGENEOUS EMULSIFIED LPs HAVE BEEN PROCESSED WITH 13M HAN AS THE DISPERSED OXIDIZING PHASE
- DISPERSED PHASE OXIDIZER PARTICLE SIZE RANGE IS TAILORABLE WITHIN WIDE LIMITS
- A ROTOR-IN-STATOR HOMOGENIZER WITH SPEED CONTROL IS SUITABLE FOR PREPARING LABORATORY LOTS UP TO 0.5 LITER
- THEORETICAL IMPETUS LEVELS EQUAL TO OR GREATER THAN SOLUTION MONOPROPELLANT LGP 1845 ARE EASILY ACHIEVABLE FOR 13M HAN/COMMERCIALLY AVAILABLE HYDROCARBONS, FOR SLIGHTLY FUEL RICH FORMULATIONS

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

CONCLUSIONS (CONT'D)

- SELECTED HETEROGENEOUS EMULSIONS DEMONSTRATE INSENSITIVITY TO IMPACT, EXCEPT FOR THE FORMULATION BASED ON BDNPA-F ENERGETIC NITROPLASTICIZER
- EMULSIFIED LPs ARE PSEUDOPLASTIC IN FLOW BEHAVIOR, SEVERAL DEMONSTRATING THIXOTROPY. THEY ARE READILY PUMPED THROUGH A GUN VALVE AT PRESSURES TYPICAL OF LPG SYSTEMS, I.E., 500 PSIG

PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.

RECOMMENDATIONS FOR ADDITIONAL CHARACTERIZATION

- ADDITIONAL PHYSICAL PROPERTIES CHARACTERIZATION
  - DENSITY
  - TIME DEPENDENT THIXOTROPY OF SHEARED PROPELLANT SAMPLES
  - DROPLET SIZE DISTRIBUTION OF SHEARED PROPELLANT SAMPLES
  - FREEZING POINT
- COMBUSTION PERFORMANCE IN A CLOSED BOMB TYPE APPARATUS
- IGNITABILITY CHARACTERIZATION USING PYROGENIC IGNITION SOURCE
- FLOW AND COMBUSTION DIAGNOSTICS IN A HIGH PRESSURE ENVIRONMENT, SIMULATING 30mm RLPG FLOW RATES
- 20mm MANN BARREL TESTS UTILIZING STANDARD, 20mm CASED CARTRIDGE AND PROOF SLUG WITH TAILORED IGNITION SYSTEM
- FORMULATION TAILORING FOR HIGH PERFORMANCE SYSTEMS

THE DIFFUSION AND MIXING CHARACTERISTICS OF LGP 1845 AND WATER

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U.S. Army Ballistic Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ABSTRACT

An approximate value for the diffusion coefficient of liquid gun propellant (LGP) 1845 into water was obtained using a two color mixing method. The two components, water and propellant, were dyed separate colors and the mixing region was measured as a function of time. Using the experimental mixing length, the diffusion coefficient was calculated. As a check on the procedure, methanol and glycerine were also tested. The diffusion values obtained in the experiments for methanol and glycerine were 1.28E^{-5} cm^2/s and 1.73E^{-5} cm^2/s, respectively. The diffusion coefficient for LGP 1845 into water is 1.59E^{-5} cm^2/s. A prediction for the diffusion coefficient of hydroxylammonium nitrate into water was also calculated and found to be 1.4E^{-5} cm^2/s. The short term mixing characteristics of LGP and water was also investigated. The results indicated that the propellant and water will not mix properly unless agitated.

THE DIFFUSION AND MIXING CHARACTERISTICS OF LGP 1845 INTO WATER

CRIS WATSON & JOHN D. KNAPTON

U.S. ARMY ALLISTIC RESEARCH LABORATORY

OUTLINE

OBJECTIVE

EXPERIMENTAL APPROACH

EQUATIONS

DIFFUSION RESULTS

MIXING CHARACTERISTICS

SUMMARY

OBJECTIVE

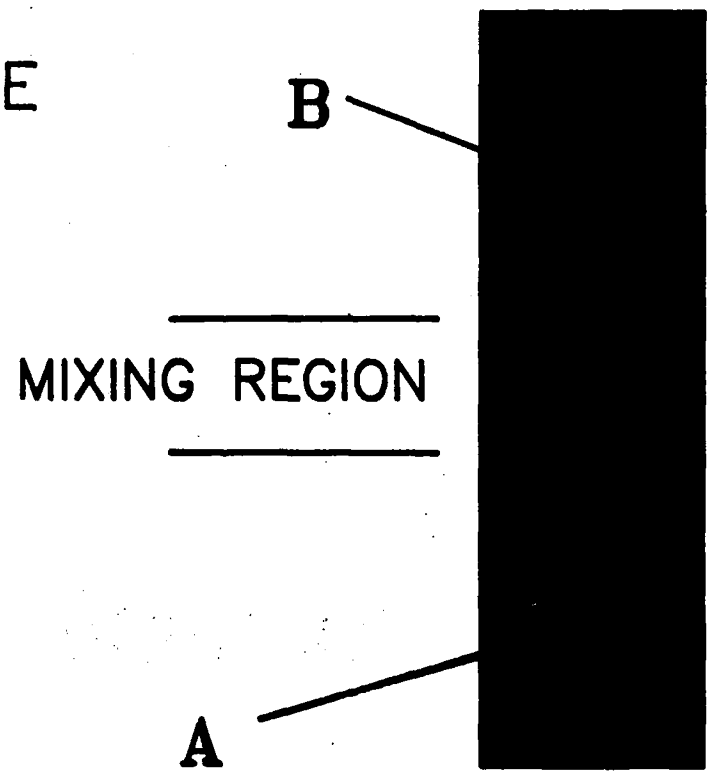
DETERMINE THE DIFFUSION COEFFICIENT AND EXPLORE THE MIXING CHARACTERISTICS OF A HAN-BASED LIQUID MONOPROPELLANT INTO WATER

EXPERIMENTAL APPROACH

TWO COLOR
MIXING TECHNIQUE

LGP 1845

STANDARDS
METHANOL
GLYCERIN



EQUATIONS

FICK'S RATE EQUATION:

$$J(a,b) = - D(a,b) \; \rho \frac{d\,W(a)}{d\,Z}$$

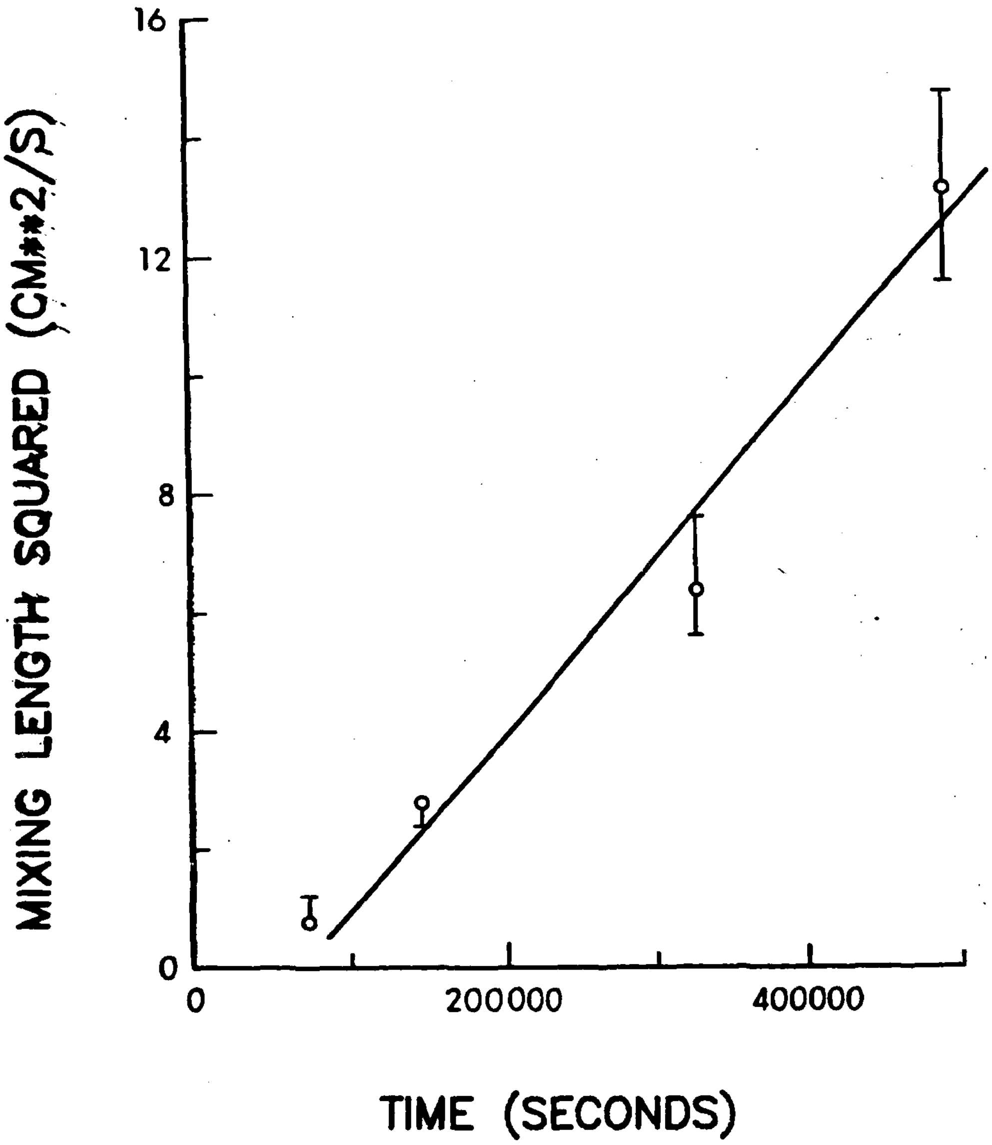
$$\vdots$$

$$D\,(a,b) = + \frac{\rho_a \, \Delta Z^2}{(\rho_a + \rho_b)\, \Delta T}$$

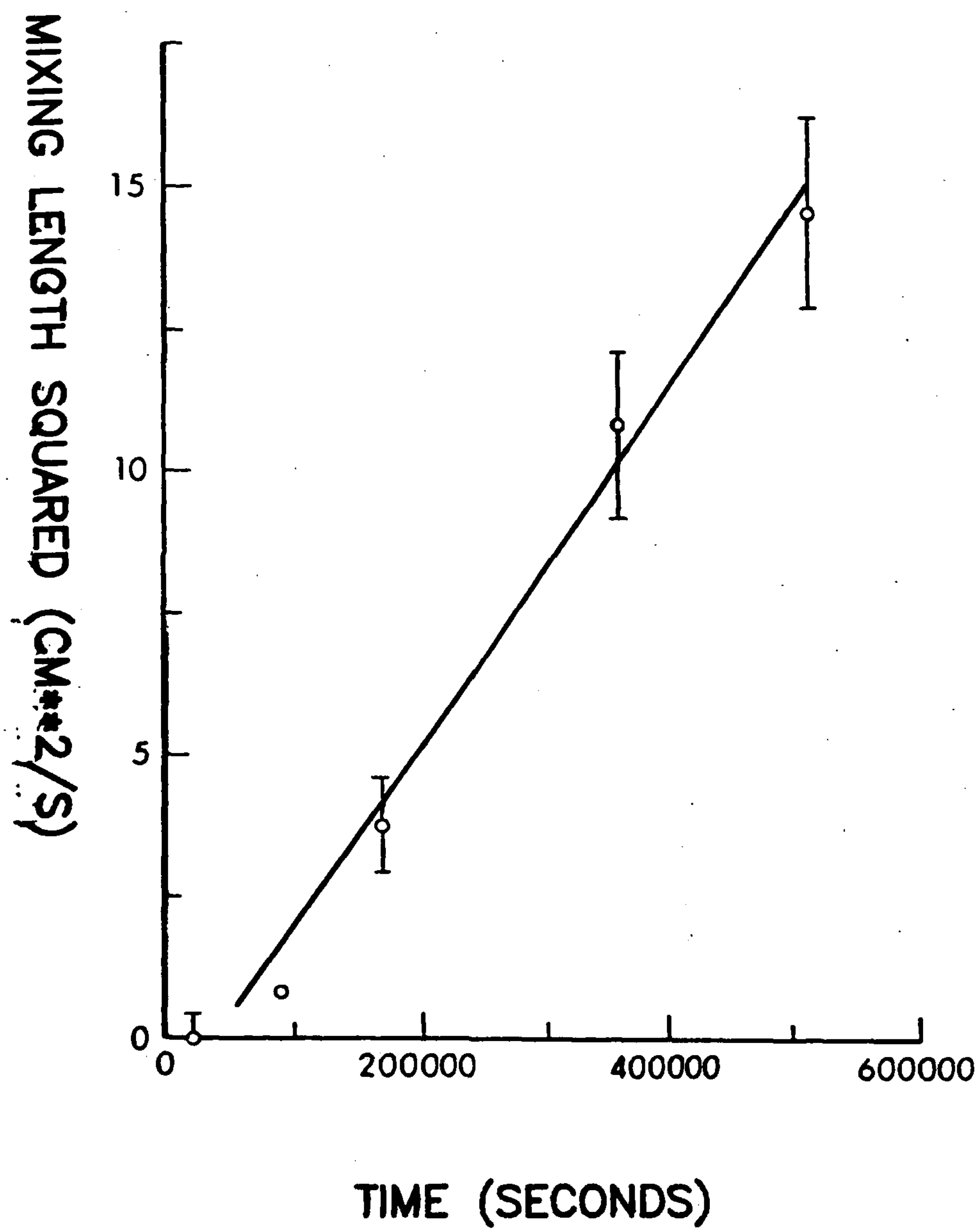
PREDICTION:

$$D = (8.93E-10) * T_o \left(\frac{l_-^o * l_+^o}{\Lambda_o} \right) \left(\frac{(z^+ + z^-)}{(z^+ * z^-)} \right)$$

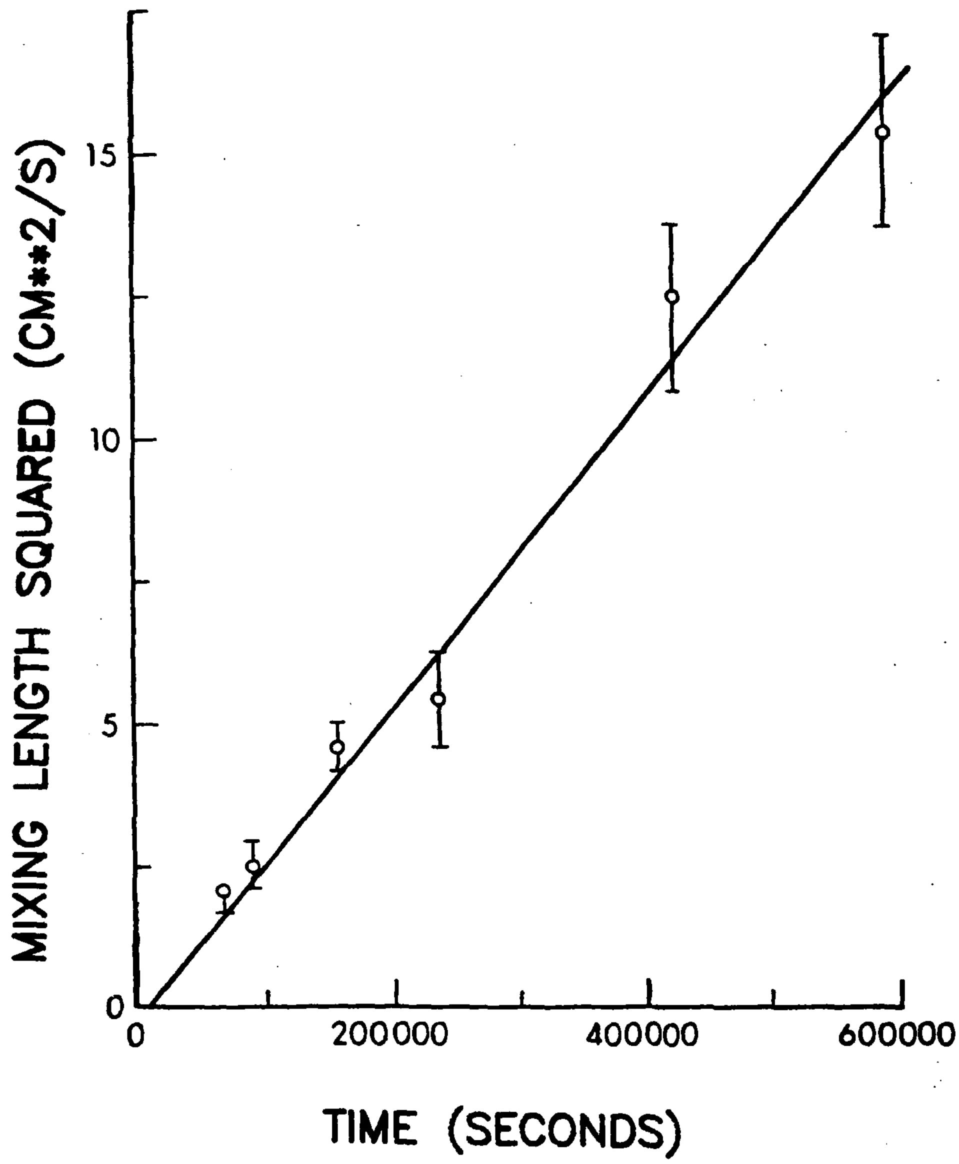
EXPERIMENTAL RESULTS FOR METHANOL



EXPERIMENTAL RESULTS FOR GLYCERIN



EXPERIMENTAL RESULTS FOR LGP 1845



DIFFUSION EXPERIMENT RESULTS

TEST LIQUID	DIFFUSION COEFFICIENT (CM^2/S)	
	BOOK VALUE	EMPIRICAL
LGP 1845	N/A	1.59 E−5
METHANOL	1.28 E−5	1.23 E−5
GLYCERIN	0.94 E−5	1.73 E−5
		PREDICTED
HAN *	N/A	1.43 E−5

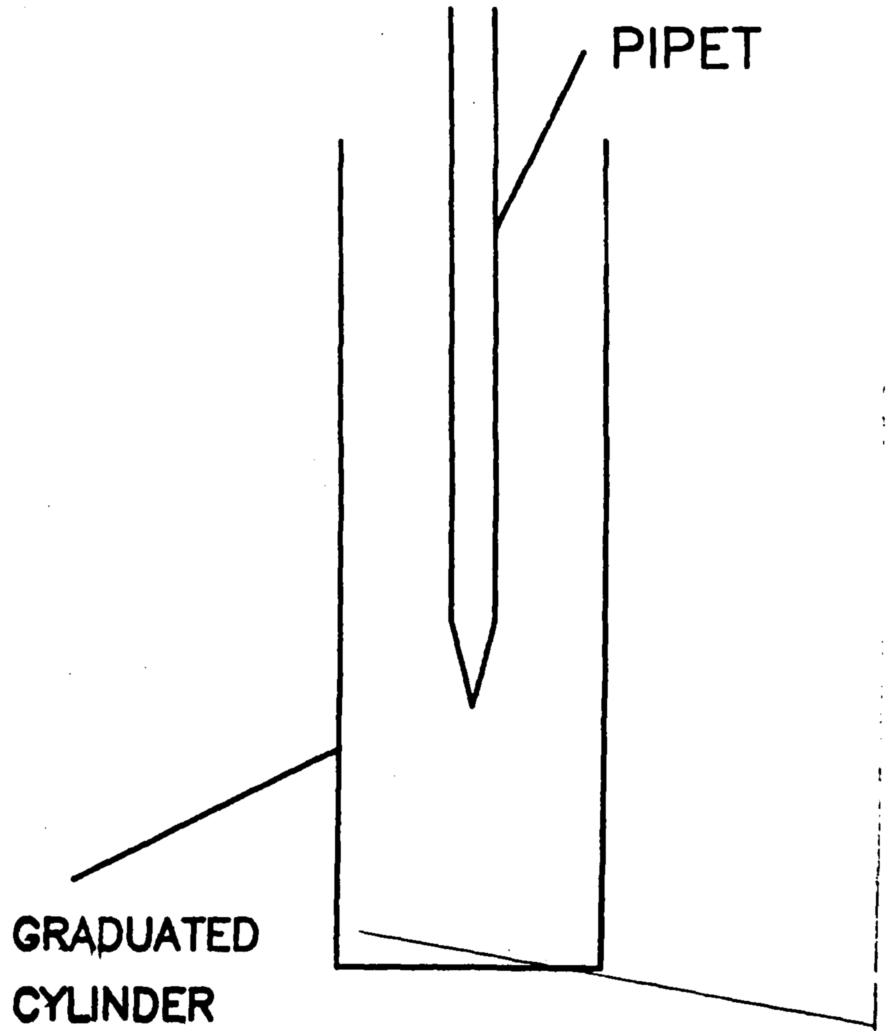
* AT INFINITE DILUTION

EXPERIMENTAL SETUP

1. WATER INTO LP
   AT THE BOTTOM

2. WATER INTO LP
   AT THE MIDDLE

3. LP INTO WATER
   AT THE MIDDLE



Physical Properties of Liquid Propellants With Dissolved Gases

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ABSTRACT

The solubility of three important gases (argon, nitrogen, and methane) has been estimated in liquid propellants using an extended corresponding states theory, and some recently obtained experimental data of Koski (see following abstract), over a range of temperatures, for pressures up to 1000 bars. The effect of these dissolved gases on physical properties such as surface tension are then estimated.

The solubility of the gases have been estimated by using the fundamental equation.

$$f^{(G)} = x \gamma^* H^o \exp\left[\int \bar{V} / RT \, dP\right]$$

where $f^{(G)}$ is the fugacity of the gas phase, x, the mole fraction of the dissolved gas in the propellant, and γ^*, H^o, V, are the activity coefficient, Henry's constant, and partial molar volumes respectively of the dissolved gas in the liquid propellant. The values of $f^{(G)}$, γ^*, H^o, and V are then estimated using the corresponding states theory, and limited experimental data. This technique can also be easily extended to examine mixtures of gases in liquid propellants.

After the solubilities of the gases in liquid propellants have been estimated, they can be used to estimate their effect on various physical properties, such as density, surface tension, etc. We will show some of our results for surface tension of liquid propellants under pressure, and compare the results with those obtained when gas solubilities are ignored.

SOLUBILITY OF GASES IN LP 1846

Walter S. Koski
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The solubility of various gases has been measured in LP 1846 using chromatographic techniques. The temperature range for most of the gases was from -15^{o} to $30^{o}C$ in 5 degree intervals. The order of increasing gas solubilities was nitrogen, oxygen, argon, methane, hrypton, and xenon. These measurements permitted the determination of the free energy, enthalpy, and entropy changes for the solution process. The behavior of oxygen was anomalous since it apparently slowly reacts with the hyudroxylammonium ion to produce N_2O.

APPENDIX A

CONFERENCE ON HAN-BASED LIQUID PROPELLANT FLAMES, PROPERTIES, AND STRUCTURE

Final Program

All sessions will be held in Bldg 330.

Tuesday, 25 August

8:30 am	WELCOME. Walter F. Morrison, Program Manager, LP Program
8:40 am	ARRANGEMENTS & SIMILAR FOLDEROL. Eli Freedman, ABCB, BRL

SESSION I: Nathan Klein, BRL, presiding

8:45 am	THE PHASE DIAGRAM OF HAN-WATER. J. Bevan Ott, Brigham Young University
9:30 am	DIFFRACTION STUDIES OF HAN. Fred Ross, University of Missouri at Columbia
10:15 am	break
10:45 am	HIGH PRESSURE SPECTROSCOPY AND THE STRUCTURE OF HAN. Mark Davies and Robert A. Fifer, BRL
11:15 am	RAMAN SPECTROSCOPY OF AQUEOUS SOLUTIONS AT HIGH TEMPERATURES AND PRESSURES. Peter Spohn and T.B. Brill, Univ of Delaware
11:45	Lunch

SESSION II: Josephine Wojciechowski, BRL, presiding

1:30 pm	EQUATION OF STATE OF HAN SOLUTIONS. Julius Frankel, BWL
2:00 pm	EXPLOSIVE VAPORIZATION OF INDUCED BY LASER RADIATION ON A WATER DROPLET CONTAINING NITRATE. David Leach and R.K. Chang, Yale University
2:30 pm	break
3:00 pm	DROPLET COMBUSTION OF HAN-BASED LIQUID PROPELLANTS. C.K. Law, University of California, Davis.
3:45 pm	adjourn

Wednesday, 26 August

SESSION III: Madelyn M. Decker, BRL, presiding

8:30 am	DSC OF LIQUID PROPELLANTS AND CRYSTALLINE HAN. Leon Decker and R.A. Fifer, BRL
9:00 am	DECOMPOSITION STUDIES OF LP 1845. James T. Cronin and T.B. Brill, University of Delaware
9:30 am	STABILITY CHARACTERISTICS OF DEFLAGRATING LIQUID PROPELLANTS. R.C. Armstrong and S.R. Vosen, Sandia Labs
10:00 am	break
10:30 am	THE COMBUSTION OF HAN-BASED LIQUID PROPELLANTS. S.R. Vosen, Sandia Labs
11:00 am	A LIQUID PROPELLANT DECOMPOSITION/REACTION MODEL. H.A. Dwyer and B.R. Sanders, Sandia Labs
11:30 am	STABILIZATION OF HAN SOLUTIONS AGAINST TRANSITION METAL ION IMPURTIES. Richard C. Thompson, Univ of Missouri--Columbia
12:00	lunch

SESSION IV: Charles S. Leveritt, BRL, presiding

1:30 pm	ELECTROCHEMICAL STUDIES RELATED TO HAN. R.L. Dotson, Olin Corp.
2:00 pm	PRELIMINARY STRAND-BURNING RATES FOR HAN-BASED GELLED PROPELLANTS. D.S. Chiu, ARDEC
2:30 pm	break
3:00 pm	EMULSIFIED HAN-BASED PROPELLANTS. Neale Messina, PCRL
3:30 pm	DIFFUSION STUDIES IN LP 1846. Cris Watson, BRL
4:00 pm	adjourn
6:30 pm	DINNER

Thursday, 27 August

SESSION V: Eli Freedman, BRL, presiding

8:30 am	PHYSICAL PROPERTIES OF LIQUID PROPELLANTS WITH DISSOLVED GASES. Sohail Murad, University of Illinois at Chicago
9:00 am	SOLUBILITY OF GASES IN LP 1846. Walter Koski, JHU
9:30 am	A NEW DETERMINATION OF THE ENTHALPY OF COMBUSTION OF TRIETHANOLAMMONIUM NITRATE. Jennifer C. Colbert and Eugene S. Domalski, US National Bureau of Standards
10:00 am	break
10:15 am	GENERAL DISCUSSION
12:00	Final Adjournment

APPENDIX B

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